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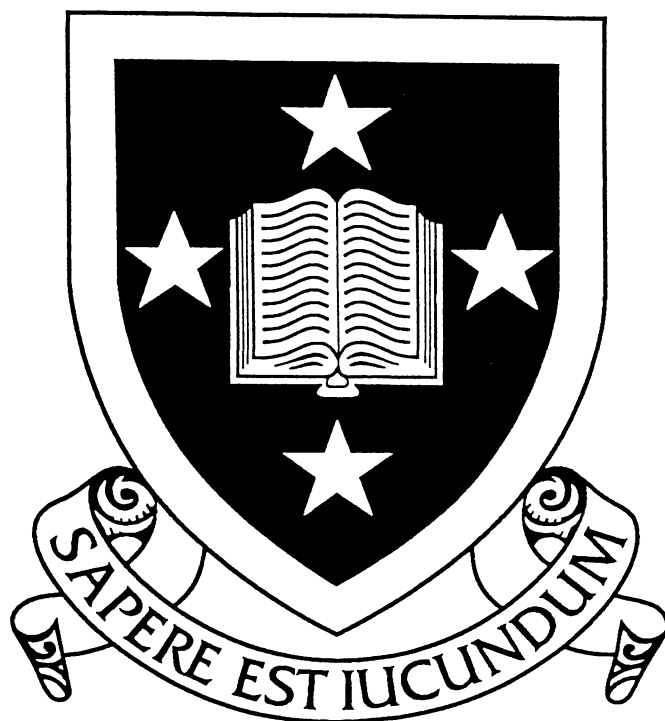
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ORGANOMETALLIC CHEMISTRY
OF ARSENIC, PHOSPHORUS
AND OTHER SYSTEMS



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ABSTRACT

Arsenic hydride and antimony hydride reactions with iron carbonyls were investigated and compared to analogous reactions using germanium hydrides.

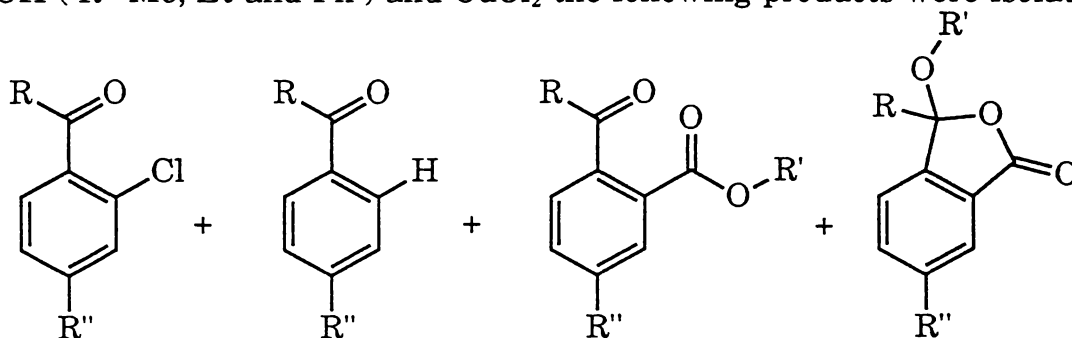
The reaction between arsane and $\text{Fe}(\text{CO})_5$ is a new, higher yielding synthesis of $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$. The reaction between arsane and $\text{Fe}_2(\text{CO})_9$ led to the new cluster $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$. Characterisation was by an X-ray crystal structure determination. $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ crystallises in the orthorhombic space group Pbca , with unit cell parameters $a = 22.908(7)$, $b = 17.521(9)$, $c = 16.071(7)$ Å and $Z = 8$. This cluster consists of four AsFe_2 triangles linked by arsenic vertices and an iron-iron edge. In an attempt to prepare similar antimony clusters, stibane was reacted with $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$, but no analogues were isolated.

The β -ketophosphane (2-acetylphenyl)diphenylphosphane, $\text{Ph}_2\text{P}[\text{C}_6\text{H}_4\text{COMe}]$, was prepared in a multi-step synthesis that involved; (i) coupling chlorodiphenylphosphane and 2-bromoethylbenzene, (ii) oxidation of the phosphorus with H_2O_2 , (iii) oxidation of the ethyl group with CrO_3 , and (iv) reduction at the phosphorus atom. Attempts to prepare the similar disubstituted phosphane $\text{PhP}[\text{C}_6\text{H}_4\text{COMe}]_2$, by an analogous route, instead afforded $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$ at the CrO_3 oxidation step.

The potential use of $\text{Ph}_2\text{P}[\text{C}_6\text{H}_4\text{COMe}]$ as a ligand on metal centres was demonstrated by its electron-transfer catalysed reaction with $\text{Ru}_3(\text{CO})_{12}$, which gave the expected product $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$.

Gentle heating of $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$ in heptane led to the *cyclo*-metallated cluster $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ through P-C bond cleavage. A single crystal X-ray diffraction study on $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ showed that it crystallises in the triclinic space group $\text{P}\bar{1}$ with $a = 10.200(11)$, $b = 12.084(12)$ and $c = 14.422(13)$ Å, $\alpha = 81.06(7)$, $\beta = 77.18(8)$ and $\gamma = 76.98(8)^\circ$ and $Z = 2$. The cluster is derived from $\text{Ru}_3(\text{CO})_{12}$ with three carbonyl ligands replaced by a $\mu\text{-PPh}_2$ moiety and an η^2 -2-acetylphenyl group.

The reactions between *ortho*-manganated acetophenone derivatives and various halides were investigated and compared to the analogous aryl-transfer reactions using mercury chloride. From the reaction between $\text{RC}(\text{O})\text{C}_6\text{H}_3\text{R}''\text{Mn}(\text{CO})_4$, ($\text{R}=\text{Me, OMe, Ph}$; $\text{R}''=\text{H, OMe}$), $\text{R}'\text{OH}$ ($\text{R}'=\text{Me, Et and Ph}$) and CuCl_2 the following products were isolated

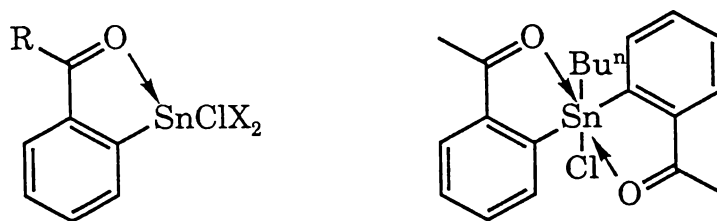


These can be explained in terms of competition between $\text{Mn-C}_{\text{aryl}}$ bond cleavage (the first two products), or in terms of CO insertion into the $\text{Mn-C}_{\text{aryl}}$ bond, with subsequent attack by the solvent (the last two products).

The reaction between $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$, and PPh_2Cl involves CO replacement to give *fac*- $[2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_3(\text{PPh}_2\text{Cl})]$ in essentially quantitative yield. Prolonged refluxing of *fac*- $[2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_3(\text{PPh}_2\text{Cl})]$ yields $\text{Mn}_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-PhPPPh})\text{-(}\mu\text{-Cl)}_2(\text{CO})_6$ in which the newly formed diphosphane ligand bridges two non-bonded manganese atoms; this compound was characterised by an

X-ray structure analysis; $P\bar{1}$ with $a = 10.980(4)$, $b = 11.756(3)$ and $c = 12.186(3)$ Å, $\alpha = 96.20(2)$, $\beta = 99.51(2)$ and $\gamma = 96.56(2)^\circ$ and $Z = 2$.

The probable products from the reaction between SnCl_2 and $2\text{-RC(O)C}_6\text{H}_4\text{HgCl}$ ($\text{R} = \text{Ph}, \text{Me}$) and from the reaction between $\text{R}_n\text{SnCl}_{4-n}$ and $2\text{-MeC(O)C}_6\text{H}_4\text{HgX}$ ($\text{R} = \text{Bu}^n$, $n = 1$, $\text{X} = \text{Cl}$; $\text{R} = \text{Ph}$, $n = 2$, $\text{X} = \text{I}$) are the acylaryltin derivatives $2\text{-RC(O)C}_6\text{H}_4\text{SnX}_2\text{Cl}$ ($\text{R} = \text{Ph}$, $\text{X} = \text{Cl}$; $\text{R} = \text{Me}$, $\text{X} = \text{Cl}, \text{Ph}$) and $[2\text{-MeC(O)C}_6\text{H}_4]_2\text{Sn}(\text{Bu}^n)\text{Cl}$ shown below



These assignments were based on ^{119}Sn and ^{13}C nmr spectroscopy.

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ABBREVIATIONS

Ac	acetyl
Az	2-C ₆ H ₄ N=NPh
Bu ⁿ	n-butyl
Bu ^t	t-butyl
DMSO	dimethylsulphoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
EPA	Electron Probe Analysis
Et	ethyl
ETC	electron-transfer catalysis
FAB	Fast Atom Bombardment
FAB-MS	Fast Atom Bombardment Mass Spectrometry
GC	Gas Chromatograph
GC-MS	Gas Chromatography Mass Spectrometry
IR	Infrared Spectroscopy
br	broad
m	medium
s	strong
sh	shoulder
vs	very strong
vw	very weak
w	weak
Me	methyl
m.p.	melting point
nmr	Nuclear Magnetic Resonance
δ	chemical shift (ppm)
d	doublet
dd	doublet of doublets
J	coupling constant (Hz)
m	multiplet
q	quartet
s	singlet
t	triplet

$w_{\frac{1}{2}}$	half band width at half peak height
Ph	phenyl
PLC	Preparative Layer Chromatography
RT	room temperature
sp	$\text{Ph}_2\text{P}(2\text{-C}_6\text{H}_4\text{CH=CH}_2)$
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
PCOH	(2-diphenylphosphino)benzaldehyde

Prologue

PROLOGUE

The initial aim of this investigation was to investigate the reactions of arsane and stibane with iron carbonyls. However, it became clear early in the study that the scope of this system was more limited than previously found, for example, with germane and silane. Consequently several other areas of organometallic chemistry were studied, as set out below.

The variety of work presented in this thesis is such that a single introductory chapter was not feasible. Each section of work, as reported in separate chapters, is self contained with its own introduction.

Chapter One of this thesis reports the general experimental methods and reagents common to all sections of work; Chapter Two describes the work performed in the arsenic and antimony hydride-iron carbonyl systems; Chapter Three reports the synthesis of a new ligand (2-acetylphenyl)diphenylphosphane, the attempted synthesis of the related bis(2-acetylphenyl)phenylphosphane, and describes the reactions of (2-acetylphenyl)diphenylphosphane with $\text{Ru}_3(\text{CO})_{12}$; in Chapter Four the oxidation reactions of (2-acetylphenyl)tetracarbonylmanganese and similar derivatives with Cu(II) is reported; and Chapter Five discusses aryl transfer reactions of (2-acetylphenyl)tetracarbonylmanganese with phosphorus, tin and aluminium halides.

Chapter One

CHAPTER ONE

EXPERIMENTAL TECHNIQUES

1.1 GENERAL EXPERIMENTAL TECHNIQUES

All glassware was washed in chromic acid or aqua regia, then in water followed by acetone. The glassware was then dried in an oven before use. The concentrated acids are used to remove any basic sites from the glass surface. These basic sites can react with the products of the reactions, leading to decomposition.

The preparation and handling of air-sensitive, highly toxic and volatile compounds, such as arsane and stibane, was carried out using conventional glass vacuum line techniques.^[1] Apiezon 'N' grease was used for stopcocks and apiezon 'M' for joints.

Many of the products and reactants involved in this work undergo oxidation and/or hydrolysis if exposed to the atmosphere. Manipulations of involatile compounds were therefore carried out in nitrogen-flushed glassware on a Schlenk line or in a glove box.

Most reactions involving volatile compounds were carried out in 50ml high pressure glass ampoules (eight atmospheres safe pressure).

These were sealed after the volatile compounds had been condensed in and left in the dark while reactions took place.

The sealed ampoules were opened inside a thick-walled rubber sleeve fitted with a tap adaptor attached to a vacuum pump. The space inside the sleeve was evacuated and the ampoule frozen down in liquid nitrogen before the top of the ampoule was broken. Any incondensable compounds in the ampoule were pumped away. The ampoule was then allowed to warm to room temperature so that the volatile components could be removed and analysed. The ampoule was then filled with dry, oxygen-free nitrogen so that the involatile products could be removed without coming into contact with the air.

1.1.1 General Work-up Procedure for a Reaction Involving a Sealed Ampoule

After the ampoule had been opened, and the incondensable gases removed, the volatile compounds were transferred onto a vacuum line and examined for the presence of unreacted gases such as arsane and stibane. The remaining solid was then removed and placed in nitrogen-flushed glassware for analysis.

The involatile products that remained were separated in most cases by utilising their different solubilities in solvents of different polarities. In most cases only dried, freshly distilled n-hexane and dichloromethane were used. However more polar solvents such as tetrahydrofuran, diethylether, acetone or, in extreme cases, acetonitrile were occasionally used.

The separation was afforded by repeated extraction of the solid products by aliquots of solvent (~10 ml), starting with the least polar solvent and working through towards the most polar until no solid remained which absorbed in the $\nu(\text{CO})$ region in the infrared spectrum.

If the compounds did not react with silica or alumina (for example bis(μ_3 -arsino)nonacarbonyltriiron, Section 2.2) then good separation was achieved by column chromatography under a nitrogen atmosphere.

1.2 INSTRUMENTAL TECHNIQUES

1.2.1 Infrared Spectroscopy

The gaseous samples were contained in a 10 cm path-length gas cell with potassium bromide windows and a cold finger for increasing small sample size and moving low volatility compounds. The routine gas spectra were recorded with a 2 cm^{-1} resolution on a Philips Pye Unicam model PU9512 spectrophotometer with a range of 4000 down to $\sim 400 \text{ cm}^{-1}$.

Spectra of involatile products were recorded as either solids or in solution with a resolution of 1 cm^{-1} , or better, on either a Digilab FTIR Model FTS-40 or a Perkin Elmer 180 Spectrophotometer. The $\nu(\text{CO})$ range of 2150 down to 1800 cm^{-1} was usually used. The $\nu(\text{CO})$ region is particularly useful for identification due to the intensity and sharpness of the bands.^[2-4] Generally little mixing is observed with other vibrational modes.

The solution spectra were recorded in a conventional solution cell, usually in n-hexane or dichloromethane, with potassium bromide windows and a 0.1 mm path-length. Solids were prepared in a glove box either as a nujol mull and placed between two 2 cm diameter potassium bromide discs, or as a KBr disk where a small amount of sample is homogeneously ground with anhydrous KBr and compressed at a pressure of 120 MPa into a disk of $\sim 0.2 \text{ mm}$ thickness.

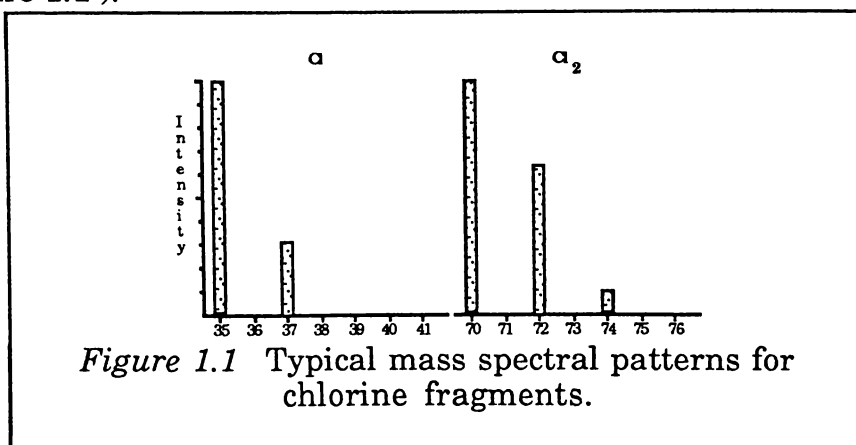
Calibration of the infrared spectrophotometers in the $\nu(\text{CO})$ region was checked to within $\pm 0.2 \text{ cm}^{-1}$ using CO .^[5]

The metal-metal stretching region ($300\text{-}150\text{cm}^{-1}$) is readily accessible using Raman spectroscopy. These absorptions usually mix with other modes of similar energy, imposing problems in both assignment and observation.^[3] These metal-metal stretches are often prominent in Raman spectra, and mixing is less of a problem when light atom ligands are involved.

1.2.2 Mass Spectrometry

Mass spectra of non-volatile solids were recorded at the University of Adelaide on a VG ZAB 2HF Fast Atom Bombardment Mass Spectrometer (FAB-MS) or on a Varian CH7 electron-impact Instrument. Mass spectra of volatile compounds were recorded at the University of Waikato on a Hewlett Packard 5890 Gas Chromatograph (GC) interfaced to a Hewlett Packard 5970 Mass Selective Detector (MS) using a 15 m HP1 non-polar column. The GC-MS was calibrated in terms of m/e values and selected fragment intensities by comparison with the standard supplied with the instrument.

The majority of organic derivatives formed were volatile and stable enough to be separated by gas chromatography before being introduced into the mass spectrometer. The presence and number of halides such as chlorine and bromine in these samples is easily recognisable and isotopic ratios give an insight into the composition of a particular ion fragment (see Figure 1.1).



Similarly for the less volatile arsenic-iron carbonyl clusters the isotopic ratios for each fragment can help distinguish between possible formulations with the same masses. The three major isotopes of iron give distinctive patterns which readily enable fragments with one, two, three or more iron atoms to be distinguished. Typical mass spectral patterns for iron are shown in Figure 1.2. In these clusters both the loss of two carbonyl fragments and of one iron atom result in a $\Delta m/e$ of 56, which can be distinguished either with high resolution mass spectroscopy or, more easily, by comparison of the ratio of the most intense peak in the envelope with that of the second most intense peak in the envelope.

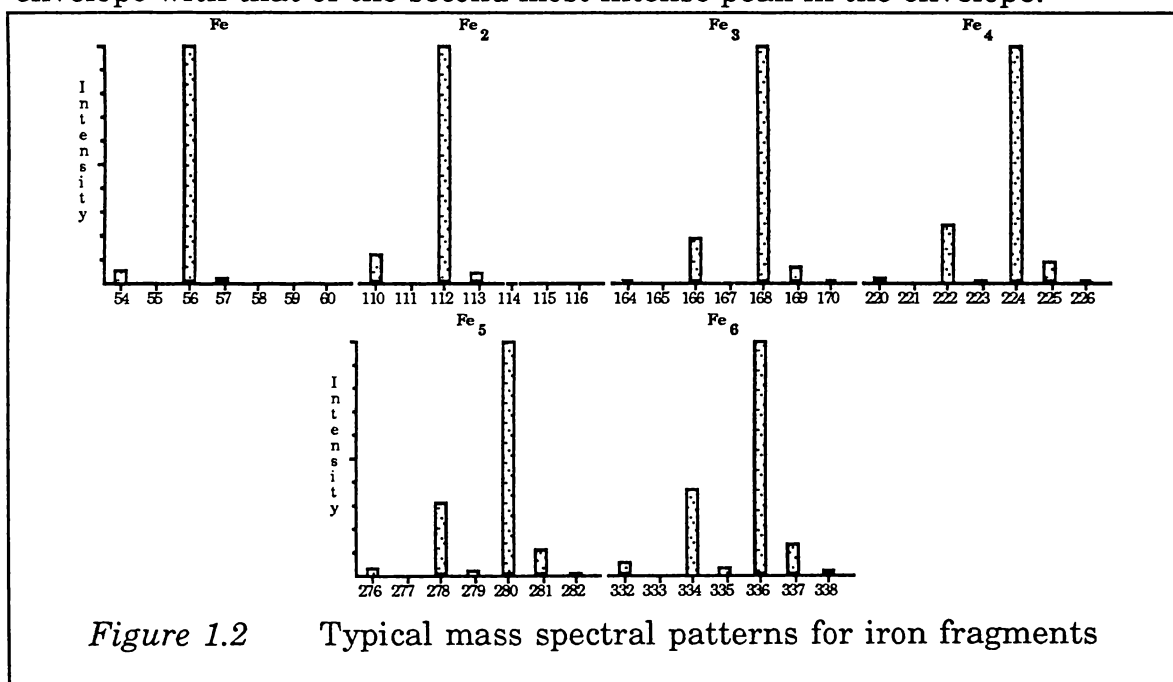
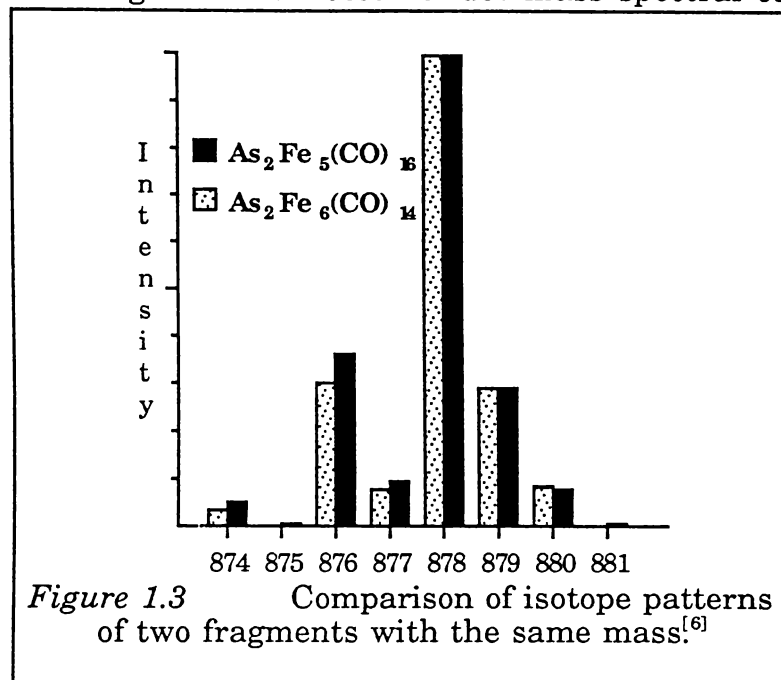


Figure 1.3 illustrates an example of this, in which the isotopic intensities of two fragments are shown. The most intense peak for both fragments, $[As_2Fe_5(CO)_{16}]^+$ and $[As_2Fe_6(CO)_{14}]^+$, would occur at a m/e of 878 e^1 however, the ratio of the 878 to the 876 peak (the second most intense peak in the envelope) for the Fe_6 fragment is 2.5 : 1 whereas for the Fe_5 fragment the same ratio is 3.3 : 1. This difference is significant enough to distinguish between the two possible formulations.

In these clusters a high proportion of the ion current is carried by fragments which retain all or part of the $E_x M_y$ skeleton, with stepwise losses of CO units, giving rise to a series of envelopes separated by 28 units. In some of the more unstable (especially thermally unstable) compounds rearrangement can occur under mass spectral conditions.



Calculation of the theoretical isotope patterns for many fragment ions can be time consuming, if not prohibitive, especially for the examples such as $As_2Fe_6(CO)^+_{14}$ and $As_2Fe_5(CO)^+_{16}$ shown above. The number of terms required to be calculated and then collected together to get the final isotope pattern is given by the following formula:

$$\text{Total number of terms} = \prod_{(\text{all elements})} (\text{number of isotopes for element})^{(\text{number of times element is in fragment})}$$

Using this formula for $As_2Fe_6(CO)^+_{14}$ (arsenic one, iron four, carbon two and oxygen three isotopes) gives a total of 3.2×10^{14} ($1^2 \times 4^6 \times 2^{14} \times 3^{14}$) terms. In reality the number of terms can be reduced substantially from this by collecting like terms as the expansion proceeds. The number of terms for any given isotope after collection of like terms is given by

Equation (1.1). The number of calculations required to compute the isotope pattern of an element in a fragment is given by Equation (1.2).

$$N_{El}(n_{El}) = n_{El} d_{El} + 1 \quad (1.1)$$

$$\begin{aligned} N_{El}^{calc}(n_{El}) &= n_{El}^{iso} \times N_{El}(n_{El}-1) + N_{El}^{calc}(n_{El}-1) \\ &= n_{El}^{iso} \times \sum_{n=1}^{n_{El}} N_{El}(n-1) \\ &= n_{El}^{iso} \times \sum_{n=1}^{n_{El}} ((n-1) d_{El} + 1) \\ &= n_{El}^{iso} \times \frac{n_{El}}{2} (2 + (n_{El}-1) d_{El}) \end{aligned} \quad (1.2)$$

where $N_{El}(n_{El})$ = number of terms for isotope pattern of $n_{El} El$
 n_{El} = number of times element El is in the fragment ion
 d_{El} = (largest isotopic Mr of element El) - (smallest isotopic Mr of element El)
 n_{El}^{iso} = number of isotopes for element
 $N_{El}^{calc}(n_{El})$ = number of calculations required to compute the isotope pattern of $n_{El} El$

The product summation of the $N_{El}^{calc}(n_{El})$ terms over all elements in the fragment will give the total number of calculations required to compute the isotope pattern of any fragment ion (equation (1.3)). Similarly the total number of terms in the final isotope pattern for a fragment ion can be obtained by summing the $N_{El}(n_{El})$ values for each element in the fragment ion as shown in Equation (1.4).

$$\begin{aligned} N_{Ion}^{calc}(Frag) &= N_{El_1}^{calc}(n_{El_1}) \times N_{El_2}^{calc}(n_{El_2}) \times \dots \times N_{El_n}^{calc}(n_{El_n}) \\ &= \prod_{El=El_1}^{El_n} (n_{El}^{iso} \times \frac{n_{El}}{2} (2 + (n_{El}-1) d_{El})) \end{aligned} \quad (1.3)$$

$$\begin{aligned} N_{Ion}(Frag) &= N_{El_1}(n_{El_1}) - 1 + N_{El_2}(n_{El_2}) - 1 + \dots + N_{El_n}(n_{El_n}) \\ &= 1 + \sum_{El=El_1}^{El_n} n_{El} d_{El} \end{aligned} \quad (1.4)$$

where $N_{Ion}(Frag)$ = number of terms for isotope pattern of ion (Frag⁺)
 $N_{Ion}^{calc}(Frag)$ = number of calculations required to compute the isotope pattern of the fragment ion (Frag⁺)

El_n = n^{th} element of the fragment ion (Frag^+)

Applying Equations (1.3) and (1.4) to $\text{As}_2\text{Fe}_6(\text{CO})_{14}^+$ gives a total of 67 ($2 \times 0 + 6 \times 4 + 14 \times 1 + 14 \times 2 + 1$) terms in the final isotope pattern requiring 6.5×10^6 calculations to compute these terms. While this is a marked reduction in the number of computations, it is still prohibitive in terms of computing by hand. Hence I developed a Macintosh based program to calculate, view and print the isotope patterns of molecular fragments. This program, Isotope Pattern Calculator^[7] (see Appendix 1), was used throughout this work to assist in assignment of mass spectral ion fragments. The final isotope pattern, as shown for $\text{As}_2\text{Fe}_6(\text{CO})_{14}^+$ in Figure 1.3, can be simplified by discarding very small terms after the final calculation.

The total number of computations can be further reduced by discarding some very small terms from the extremities of the mass range as they appear in the expansion (the reduction in number of terms by this method varies from element to element as it depends on the relative abundances of the outer mass isotopes in the element). Using this method a trade off between accuracy and speed of calculation can be achieved. The larger the terms that are considered to be zero, the less accurate the final relative intensities will be. For the example given above, to get an accuracy of $\pm 0.01 \%$ for the 100 % peak in the final isotope pattern 2721 calculations are required, whereas if the accuracy is dropped to $\pm 1 \%$ then only 419 calculations need to be computed.

1.2.3 Electron Probe Analysis (EPA)

EPA utilises a beam of high energy electrons to excite the sample by displacing core electrons. When outer higher energy electrons lose energy and fill these holes the difference in energy is emitted in the form of an X-ray. The wavelength of these X-rays can be used to determine

elemental composition and the relative intensities give an approximate ratio for the heavier elements. EPA, as used for these determinations, is not suitable for the lighter elements. Due to the very narrow excitation beam required for EPA, only very small sample sizes are required for suitable results. Several different sample areas can be scanned to test for purity and homogeneity.

Electron probe analyses were performed on an ORTEC energy-dispersive X-ray analyser attached to a JEOL model JS-M53 scanning electron microscope. The use of the software package RATIO allowed determination of elemental ratios accurate to $\pm 10\%$.

1.2.4 X-ray Diffraction

When a compound warranted a structural determination, or no other method could conclusively establish the formulation of a new compound then X-ray crystallography could provide this information if single crystals could be grown. Crystals obtained were mounted on a glass fibre using grease or, if more air sensitive, were sealed in a nitrogen flushed, thin-walled, 0.5 mm capillary tube. Preliminary precession photographs using $\text{Cu-K}\alpha$ radiation were used to check the quality of the crystal and to line up the crystal. Zero and upper level photographs, taken with Ni-filtered X-rays, were used to determine unit cell dimensions and possible space groups.

For $[\text{Fe}_2(\mu_4\text{-As})\text{Fe}_2(\text{CO})_8]_2(\text{CO})_6$, $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$, $\text{PhP}[\overline{\text{C}_6\text{H}_4\text{COO}}]_2$, $[\text{Mn}_2(\mu\text{-Cl})_2(\mu\text{-}\eta^2\text{-(Ph}_2\text{PPPh}_2)(\text{CO})_6)]$ and $[\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_6]$ full X-ray intensity data were collected at the University of Canterbury on a Nicolet model P3 four-circle automatic diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

The data were corrected for Lorentz, polarisation and absorption (either numerical or empirical) effects before solution of the structure.

The programs SHELXS86 and SHELX-76,^[8] run on a VAX model 11/780, were used for solution and refinement of the structure.

The standard deviations given for the final bond lengths and angles were calculated with respect to the quality of the data and the ratio of the parameters to the number of reflections used in the refinement. Hence they only include random errors and underestimate the effects of any systematic errors such as poor quality crystals and/or poor absorption corrections.

Care should be taken in drawing conclusions from the estimated standard deviations obtained from structural studies. Two different studies on the differences between the atom parameters in independently determined structures of the same compounds in the same space group agree well as to the average amount that the estimated standard deviations are below the true standard deviations. The first, a study by Abrahams^[9-11] had seventeen different laboratories all determine the structure of a supplied crystal of tartaric acid and found that the average standard deviation of the atom parameters was 1.41 times larger than the estimated ones. The second study by Taylor^[12] used one hundred different molecules in the Cambridge files whose crystal structure had been determined twice and determined a figure of 1.40 to 1.45. This is in remarkable agreement with the first study.

This indicates that the true standard deviations have been underestimated and that small differences in bond lengths and angles should be approached with scepticism.

1.2.5 Nuclear Magnetic Resonance Spectroscopy (nmr)

Routine ^1H , ^{13}C , ^{31}P and ^{117}Sn nmr spectroscopy was performed on a 90 MHz JEOL FX90 Multinuclear Fourier Transform spectrometer. In cases where a larger signal separation was required and for two

dimensional spectra, data were collected on a Bruker AC 300 MHz Fourier Transform spectrometer. Proton and carbon spectra were collected using a 5 mm outside diameter nmr tube using CDCl_3 , $(\text{CD}_3)_2\text{CO}$ or $(\text{CD}_3)_2\text{SO}$ depending on solubility. Spectra of other nuclei such as phosphorus and tin were recorded using 10 mm nmr tubes. These samples were dissolved in an appropriate hydrocarbon solvent with enough CDCl_3 added to obtain a lock signal. All nmr data are reported in ppm relative to tetramethylsilane for proton and carbon, 40 % H_3PO_4 for phosphorus and Me_4Sn for tin.

1.3 SOLVENTS AND REAGENTS

1.3.1 Solvents

A variety of organic solvents were used in this work for recrystallisations, extractions and reaction media:

benzene	- analytical grade reagent dried over sodium wire.
1,2-dichloroethane	- laboratory grade reagent used as supplied.
dichloromethane	- distilled under a nitrogen atmosphere from phosphorus pentoxide.
diethyl ether	- distilled under a nitrogen atmosphere from sodium/benzophenone.
n-hexane	- distilled under a nitrogen atmosphere from calcium hydride.
methanol	- distilled from magnesium/iodine and stored over molecular sieves.
30-40 petroleum spirits	- laboratory grade reagent used as supplied, referred to as petroleum spirits in the text.
acetone	- distilled from calcium chloride and stored over molecular sieves.

- tetrahydrofuran** - distilled under a nitrogen atmosphere from sodium/benzophenone.

1.3.2 Reagents

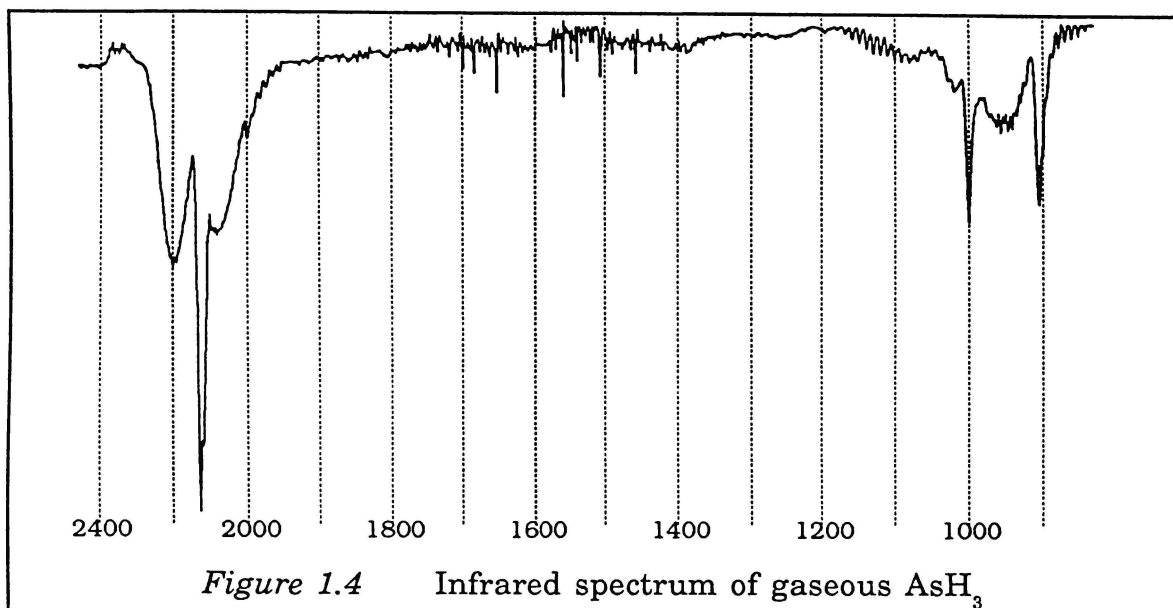
Most reagents were used as supplied:

- anhydrous SnCl_2** - prepared by refluxing the hydrate in acetic anhydride and stored over silica gel.^[13]
- anhydrous CdCl_2 ,
anhydrous CuCl_2** - prepared by refluxing the hydrate in thionyl chloride and stored over potassium hydroxide.^[14]
- $\text{Fe}_2(\text{CO})_9$,** - prepared by irradiation of $\text{Fe}(\text{CO})_5$ in glacial acetic acid.^[15]
- $\text{Fe}(\text{CO})_5$,
 $\text{Fe}_3(\text{CO})_{12}$,
 $\text{Mn}_2(\text{CO})_{10}$,** - supplied by the Pressure Chemical Company and stored under nitrogen at -20°C .

1.4 PREPARATION OF STARTING MATERIALS

1.4.1 Preparation of Arsane

AsH_3 was prepared using a variation on the procedure reported in Inorganic Synthesis^[16] which uses sulphuric acid and a basic solution of $\text{As}_2\text{O}_3/\text{KBH}_4$. The apparatus was similar to that reported but the resultant gases were passed first through a column packed with CaCl_2 and NaOH to remove water. Traps one, two and three were immersed in Dewars at: -22°C , -96°C , and -196°C to retain any remaining traces of water, As_2H_4 impurities and the desired AsH_3 respectively. Using the quantities of reactants reported,^[16] yields were typically in the range of 25 to 28 mmol which corresponds to a 51 to 57% yield based on the limiting reagent, KBH_4 . The infrared spectrum of the gaseous AsH_3 , shown in Figure 1.4, produced by this preparation corresponds well with that reported.^[16]



1.4.2 Preparation of Stibane

SbH_3 was prepared by modification of the method described by Drake.^[16] Traps one, two and three were immersed in Dewars at: -96°C , -127°C , and -196°C to retain any remaining traces of water, the desired SbH_3 and traces of SbH_3 respectively. All solutions were degassed prior to use to remove CO_2 and oxygen. A 250 ml 3-necked flask was charged with water (40 ml) and concentrated H_2SO_4 (5 ml). KOH (2 g, 50 mmol), $\text{KSbC}_4\text{H}_4\text{O}_{7.5}\text{H}_2\text{O}$ (3 g, 9 mmol) and KBH_4 (0.75 g, 14 mmol) were dissolved in that order in water (20 ml). This was added dropwise to the sulphuric acid solution over a period of five to ten minutes opening the tap to the vacuum pump occasionally to remove any hydrogen that had formed. The reaction vessel was left open to the traps for twenty minutes after all the basic antimony solution had been added to the acid, pumping every five minutes for a few seconds. Yields of SbH_3 were typically in the range of 8 to 9 mmol which corresponds to a 89 to 100% yield based on the limiting reagent, $\text{KSbC}_4\text{H}_4\text{O}_{7.5}\text{H}_2\text{O}$. The infrared spectrum of the gaseous SbH_3 , shown in Figure 1.5, produced by this preparation corresponds well with that reported.^[17]

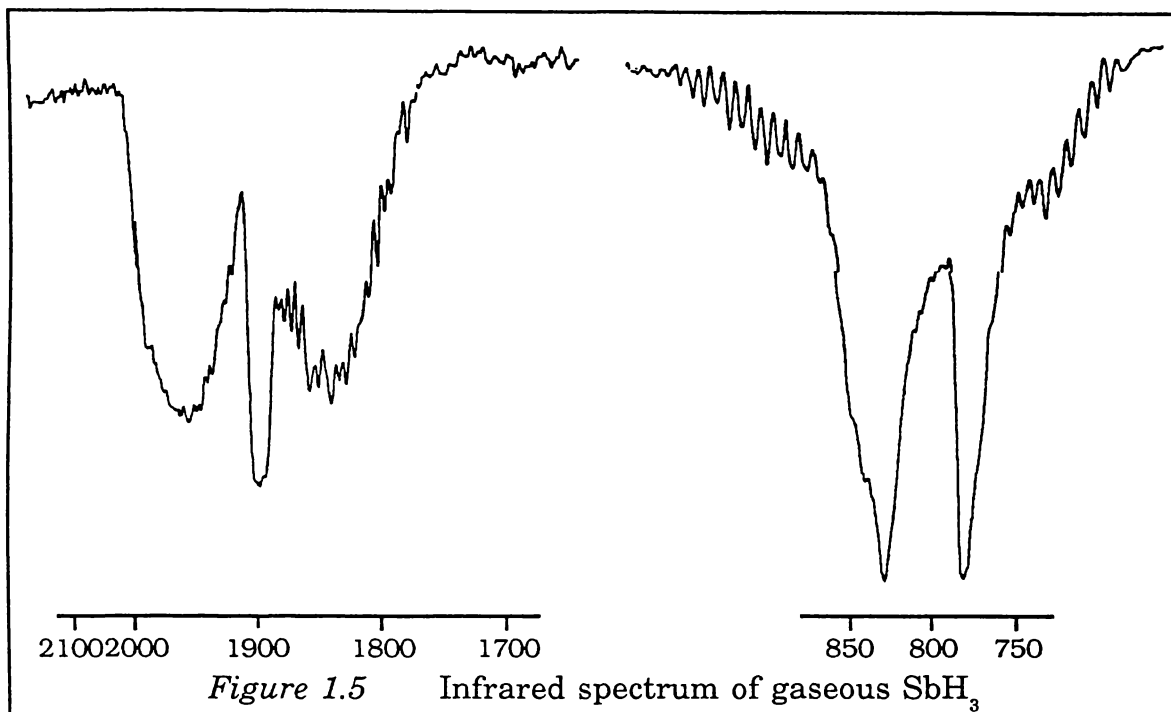


Figure 1.5 Infrared spectrum of gaseous SbH_3

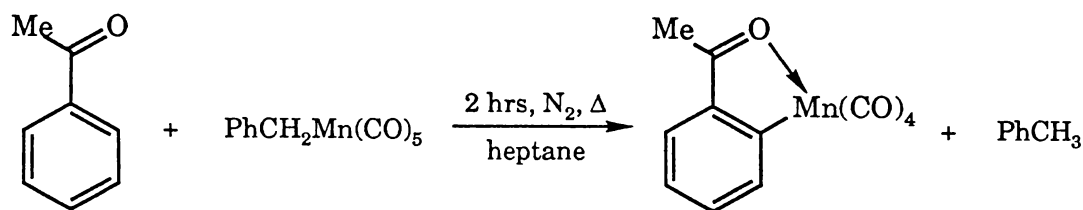
1.4.3 Preparation of Benzyl Pentacarbonyl Manganese

The standard method for the preparation of $\text{PhCH}_2\text{Mn}(\text{CO})_5$ is as described by Closson *et al.*^[17] A typical preparation was as follows.

Dried THF (60 ml) was syringed into a Schlenk flask with Na/Hg amalgam (55 g, 0.7 %), purged with N_2 and $\text{Mn}_2(\text{CO})_{10}$ (2.0 g, 5.13 mmol) added. The solution was stirred for 2 hours at ambient temperatures. The green $\text{NaMn}(\text{CO})_5$ solution was decanted under N_2 into a Schlenk flask containing PhCH_2Br (1.25 ml, 10.5 mmol). A white precipitate formed. The reaction mixture was stirred for 10 minutes and passed through a short silica gel column (60-120 mesh), washed with THF (2 x 20 ml). The THF was removed under vacuum to leave a yellow oil which was sublimed (1 mmHg, 50 °C) onto a cold finger to give $\text{PhCH}_2\text{Mn}(\text{CO})_5$ (2.14 g, 82 %). ^1H nmr (7.28 s 5H *H*-Ar, 2.45 s 2H *-CH*₂-), $\nu(\text{CO})_{\text{hexane}}$ (2105 s, 2010 vs br and 1990 vs br) cm^{-1} and m.p. 34.5-36 °C.

1.4.4 Preparation of η^2 -(2-Acetylphenyl) Tetracarbonyl Manganese

Cyclo-manganated compounds were prepared following the general method for *ortho*-manganation as described by Kaesz^[18] (Scheme 1.1).



Scheme 1.1

A typical preparation and purification is illustrated in the preparation of $(\eta^2\text{-2-acetylphenyl})\text{tetracarbonylmanganese}$ from acetophenone.

Acetophenone (200 μl , 1.5 mmol) and $\text{PhCH}_2\text{Mn(CO)}_5$ (0.46 g, 1.6 mmol) were dissolved in freshly distilled 80-100 $^\circ\text{C}$ petroleum spirit (60 ml) and the solution degassed and flushed with N_2 several times. After refluxing for 2 hours under N_2 the solvent was removed under vacuum, and the resultant yellow solid dissolved in CH_2Cl_2 (5 ml). Deactivated neutral alumina (5 g, activity IV, 10 % added H_2O) was added and the mixture shaken vigorously while the CH_2Cl_2 was evaporated under vacuum. The absorbed product was transferred onto a neutral alumina column (2 x 15 cm, activity IV). Elution with hexane removed a trace of unreacted $\text{PhCH}_2\text{Mn(CO)}_5$ and with CH_2Cl_2 a thick bright yellow band of $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\overline{\text{Mn}}(\text{CO})_4$ was collected (0.326 g, 76 %).

1.4.5 Preparation of $(\eta^2\text{-2-Acetylphenyl})$ Chloro Mercury(II)

$(\eta^2\text{-2-acetylphenyl})\text{chloromercury(II)}$ was prepared using the general method described by Cooney^[19]

$2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\overline{\text{Mn}}(\text{CO})_4$ (1.005 g, 3.50 mmol) and HgCl_2 (0.950 g, 3.50 mmol) were refluxed in methanol (20 ml) for three hours. The cold mixture was filtered, washed with cold methanol and the white

precipitate air-dried to give 2-MeC(O)C₆H₄HgCl (0.59 g, 47 %). ¹H nmr (d₆-acetone) (7.5-8.4 *m* 4*H* *H*-Ar, 2.86 *s* 3*H* -COCH₃), ¹³C nmr (d₆-acetone/d₆-DMSO) (201.1 *s* C=O, 150.0 *s* Hg-C, 141.2 *s* 1-C, 138.3 *d*, 133.9 *d*, 131.7 *d*, 128.7 *d*) and m.p. 215-217 °C.

1.4.6 Preparation of Sodium Diphenylketyl Solution

The general procedure for the preparation of Na[Ph₂CO] solution is as described by Bruce and co-workers.^[20] A typical solution was prepared as below.

To benzophenone (0.091 g, 0.5 mmol) dissolved in freshly distilled, deoxygenated THF (20 ml) in a Schlenk flask was added finely cut sodium metal (*ca.* 0.5 g). The mixture was stirred for 2 hours. The resulting deep-purple solution was assumed to be *ca.* 0.025 mol l⁻¹ in [Ph₂CO]^{•-}.

Na[Ph₂CO] solution is very reactive, and is decolourised by air or traces of water and alcohols. The solution should therefore be kept under nitrogen at all times. Aliquots^[65] may be removed using a dry, nitrogen flushed syringe. Under these conditions, the solution appears stable for several days.

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Chapter Two

CHAPTER TWO

REACTIONS OF ARSENIC AND ANTIMONY HYDRIDES WITH IRON CARBONYLS

2.1 INTRODUCTION

Over the last twenty five years, hundreds of iron clusters containing group fifteen elements have been isolated and characterised.^[1] The majority of these contain phosphorus. Of the remaining relatively small number of clusters which contain the heavier group fifteen elements: arsenic, antimony and bismuth, very few contain bare group fifteen elements, and only a small fraction of these contain arsenic.

Earlier work^[2,3] has shown that the arsenic hydrides, arsane and methylarsane, react with dicobalt octacarbonyl to yield arsenic-cobalt clusters similar to those obtained from the analogous reactions of germanium hydrides with dicobalt octacarbonyl. If the same parallels exist in the iron carbonyl system then the reactions of iron carbonyls with arsane should lead to a number of new bare arsenic-iron-carbonyl clusters.

The bare heavy group fifteen iron carbonyl clusters that are already known fall into three main groups; the first consists of μ_3 -E where

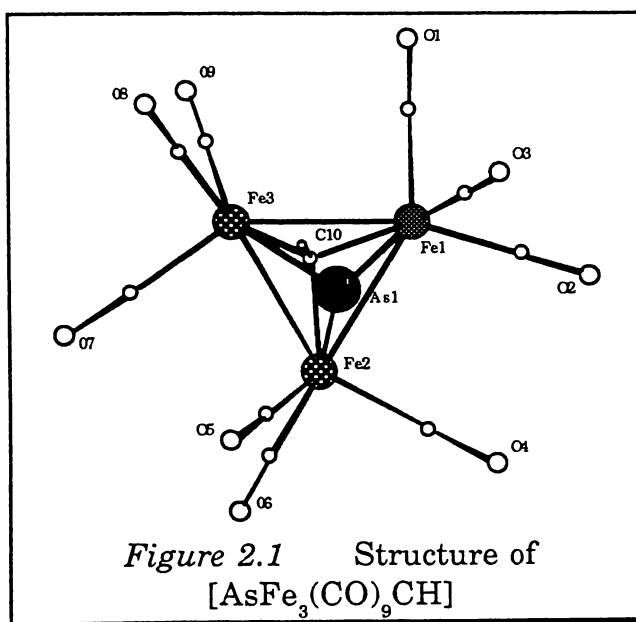
the group fifteen element face-bridges a triiron triangle; the second consists of μ_4 -E where the group fifteen element face-bridges a tetrairon quadrilateral; and the third consists of μ_4 -E where the group fifteen element edge-bridges two iron-iron bonds.

Table 2.1 Covalent Radii of Group Fourteen and Group Fifteen Atoms (pm) ^[4]									
C	77	Si	111	Ge	122	Sn	141	Pb	147
N	75	P	106	As	120	Sb	140	Bi	146

At this stage there are no known clusters which contain a bare arsenic atom bridging two iron-iron bonds, although there are a number of arsenic clusters of the other two types. The capping of a metal triangle with a main group atom is not limited by the size of the heteroatom. There are examples of such clusters with heteroatoms ranging from carbon to bismuth (see Table 2.1 for covalent radii).

2.1.1 Iron Clusters Containing a Single Arsenic Atom

2.1.1.1 μ_3 -As iron clusters

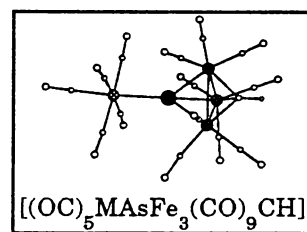


The structure of the trigonal bipyramidal cluster $[(\mu_3\text{-As})\text{Fe}_3(\text{CO})_9(\mu_3\text{-CH})]$ (**1a**), as determined by X-ray crystallography, is shown in Figure 2.1. It is isolated, somewhat surprisingly considering the mild conditions, from the reaction between arsenic metal and the carbido cluster $[\text{Fe}_5\text{C}(\text{CO})_{15}]$ in hot toluene in the presence of water or sulphuric acid.

(1a) consists of a triangle of iron atoms triply-bridged by an arsenic atom on one side and by a methyne group on the other.^[5] The iron-iron bond lengths (257_{av} pm) are somewhat shorter than the corresponding bond lengths in $[\text{Fe}_3(\text{CO})_{12}]$ (263_{av} pm)^[6] and $[\text{HFe}_3(\text{CO})_{11}]^-$ (262_{av} pm)^[7] due to the presence of the triply-bridging methyne ligand but somewhat longer than those found in $[\text{Fe}_3(\text{CO})_{10}(\mu_3\text{-CH})]^-$ ($255.4(10)$ pm)^[8] This is to be expected as the cluster also needs to accommodate the large bridging arsenic atom. The arsenic-iron bond lengths (237_{av} pm) are essentially the same as those found in other arsenic-iron clusters.^[9] This compound is isoelectronic with the trigonal bipyramidal derivative of triiron dodecacarbonyl, $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$, described later.

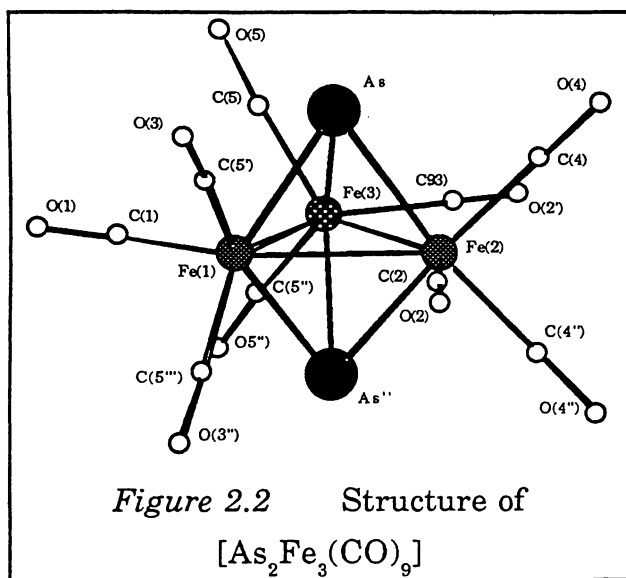
2.1.1.2 $\mu_4\text{-As}$ iron clusters

The Lewis basicity of the arsenic atom on the previously discussed $[(\mu_3\text{-As})\text{Fe}_3(\text{CO})_9(\mu_3\text{-CH})]$ is demonstrated by treating it with $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) or $[(\text{C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{THF}]$. This gives rise to the clusters $[\text{M}(\text{CO})_5\text{AsFe}_3(\text{CO})_9\text{CH}]$ ($\text{M} = \text{Cr}$ (2a), Mo (2b), W (2c)) or $[(\text{C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{AsFe}_3(\text{CO})_9\text{CH}]$ (3a) respectively, which all contain an arsenic atom bridging the face of an Fe_3 triangle and terminally bonded to the remaining metal atom.^[5] The cluster (2a) was characterised by X-ray crystallography and the remaining clusters by spectroscopic means. As with other clusters where the apical group 15 atom bonds to a fourth metal atom the iron-iron bond lengths of (2a) (259.7_{av} pm) are longer than those found in the unsubstituted cluster (1a) and the arsenic-iron bond lengths (235.4_{av} pm) are shorter. This is hardly surprising as the arsenic-iron bonding orbitals are formally increasing in s character on going from the unsubstituted to the substituted arsenic cluster. This increase in s character, both opens out the iron-arsenic-iron bond angles thus increasing the iron-iron bond lengths and shortens the arsenic-iron bond lengths.



2.1.2 Iron Clusters Containing Multiple Arsenic Atoms

One of the simplest of these clusters, $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ (**4a**), was isolated in very low yield from the reaction between trifluoroarsane and pentacarbonyliron in benzene.^[9] $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ has been shown crystallographically to consist of a triiron triangle capped on both sides by an arsenic atom to give a trigonal bipyramidal type structure with the two arsenic atoms in the apical positions (see Figure 2.2). The structure



consists of two orientations of the molecule distributed equally and randomly throughout the crystal lattice. The nine oxygen atoms are nearly coincident in both orientations, hence the placing of one molecule in either orientation in the unit cell makes little difference sterically to the

neighbouring molecules. The iron-iron bond lengths in (**4a**) (262_{av} pm) are longer than those found in (**1a**) . This is to be expected due to the larger covalent radius of the bridging arsenic atom compared to the $\mu_3\text{-CH}$ group in (**1a**).

When (**1a**) is treated with $[\text{M}(\text{CO})_5\text{THF}]$ ($\text{M} = \text{Cr}, \text{Mo}$) the cluster acts as a Lewis acid to give the clusters $[\text{M}(\text{CO})_4\{\text{AsFe}_3(\text{CO})_9\text{CH}\}_2]$ ($\text{M} = \text{Cr}$ (**5a**), Mo (**5b**)), which all contain two arsenic atoms bridging the face of two different Fe_3 triangles and terminally bonded to the introduced heteroatom.^[5]

2.1.3 Iron Clusters Containing a Single Antimony or Bismuth Atom

In contrast to the situation with arsenic, a considerable range of iron carbonyl clusters are known to contain bare antimony or bismuth atoms.

2.1.3.1 μ_3 -E iron clusters

Many of the μ_3 -E iron clusters are inter-related by oxidation, reduction and acidification processes. The reaction between sodium bismuthate and methanolic iron carbonyl affords the anionic cluster $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})]^-$ (**6**) which, like the isoelectronic cluster (**1a**), contains a tetrahedral BiFe_3 core.^[10] The neutral cluster, $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-COMe})]$ (**7**),^[11] is produced when (**6**) is slowly methylated with $\text{CH}_3\text{SO}_3\text{CF}_3$ in dichloromethane solvent. Methylation of the anionic cluster (**6**) does not effect the length of the bismuth-iron bonds (265.0_{av} pm in $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})]^-$ and 265.0_{av} pm in $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-COMe})]$). The iron-iron distances observed in both clusters are not statistically different either ($264.2(6)_{\text{av}}$ pm in (**6**) and $262.2(21)_{\text{av}}$ pm in (**7**)). Unlike the trends observed for $[\text{Fe}_4(\text{CO})_{13}]^{[12]}$ the iron- μ_3 -CO distances are virtually unchanged upon methylation (207.4_{av} for (**7**) and 207.2_{av} for (**6**)). Cluster (**6**) is also prepared by oxidation of the trianionic species $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ while acidification of $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ in aqueous methanol yields the hydrido cluster $[\text{BiFe}_3(\text{CO})_9(\mu\text{-H})_3]$ (**8**).^[11]

Cluster (**8**) consists of a triangular Fe_3 core triply-bridged by a single bismuth atom with a hydride ligand bridging each iron-iron bond. The bismuth-iron bond lengths (263.9_{av} pm) are similar to those found in the methyne cluster (**1c**). The iron-iron distances (277.4_{av} pm), which are significantly longer in (**8**) than in (**1c**) probably due to the influence of the hydride ligands in some sort of three centre bond, are comparable to those found in the more sterically demanding $[(\mu_3\text{-Bi})_2\text{Fe}_3(\text{CO})_9]$ cluster (see

later). The structurally related trigonal bipyramidal clusters $[(\mu_3\text{-E})\text{Fe}_3(\text{CO})_9(\mu_3\text{-CH})]$ (E = Sb (**1b**), Bi (**1c**)), which are isolated from the reaction between antimony trichloride or bismuth metal and the carbido cluster $[\text{Fe}_5\text{C}(\text{CO})_{15}]$ respectively, are isostructural with the arsenic analogue described above.^[5] Not too surprisingly the group 15 atom to iron bond lengths increase in going down the group from arsenic to bismuth for clusters (**1**). The iron-iron bond lengths also increase, reflecting the increasing size of the covalent radii of the group 15 atoms, in moving down the group.

The structurally characterised antimony species $[\text{Sb}\{\text{Fe}(\text{CO})_2\text{Cp}\}_3]$ (**9a**), was isolated as one of the products from the salt elimination reaction between antimony trifluoride and sodium cyclopentadienyldicarbonylferrate.^[13] The analogous bismuth species $[\text{Bi}\{\text{Fe}(\text{CO})_2\text{Cp}\}_3]$ ^[14] (**9b**), which is formed in the reaction between bismuth trichloride and three equivalents of sodium cyclopentadienyldicarbonylferrate in tetrahydrofuran, and $[\text{Bi}\{\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_4\text{Me})\}_3]$ ^[15] (**9c**) both photochemically decarbonylate to give the *closo* tetrahedral clusters $[\text{BiFe}_3\text{Cp}_9(\mu\text{-CO})_3]$ (**10b**) and $[\text{BiFe}_3(\text{C}_5\text{H}_4\text{Me})_9(\mu\text{-CO})_3]$ (**10c**) respectively.^[15,16]

The bismuth-iron bond lengths of 273.8_{av} pm found in the open complex (**9c**) are markedly longer than those found (258.3_{av} pm) in the *closo* derivative, (**10c**). This trend is common throughout cluster chemistry; an example in the cobalt system constitutes the bismuth tricobalt complexes $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ and $[\text{BiCo}_3(\text{CO})_9]$. The former open complex has bismuth-cobalt bond lengths of 276.6_{av} pm^[17] as compared to $261.3(6)$ pm^[18] for the latter *closo* cluster. The bismuth-iron bond lengths in the cyclopentadienyl cluster (**10b**) are not significantly different from the corresponding bond lengths in the methyl derivative (**10c**). The similarity of these bond lengths makes comparison of the group 15 to iron bond lengths of clusters (**9c**) (see above) and (**9a**) ($263.8(2)$ to

267.6(2) pm^[19]) valid. These bond lengths once again reflect the larger covalent radius of the bismuth atom as compared to antimony.

2.1.3.2 μ_4 -E iron clusters

The previously mentioned species $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ (**11b**) is produced when sodium bismuthate is reacted with methanolic iron carbonyl in the presence of base.^[10] The cluster (**11b**) contains a central bismuth atom tetrahedrally coordinated to four $\text{Fe}(\text{CO})_4$ moieties.^[20] The analogous antimony complex, $[\text{Sb}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ (**11a**) is synthesised^[21] from antimony trichloride or antimony pentachloride and $\text{Na}_2\text{Fe}(\text{CO})_4$ or basic, methanolic $\text{Fe}(\text{CO})_5$. The Sb-Fe bond lengths observed in cluster (**11a**) at 266.7(4)_{av} are significantly shorter than the corresponding bond lengths observed in cluster (**11b**), 275.1(3)_{av} pm. These distances correlate with the differing covalent radii of antimony and bismuth.

Sequential protonation of (**11a**) with trifluoromethanesulphonic acid results in the formation of $[\text{Fe}_3(\text{CO})_9(\mu\text{-H})\{\mu_3\text{-SbFe}(\text{CO})_4\}]^{2-}$ (**12**) and $[\text{Fe}_3(\text{CO})_9(\mu\text{-H})_2\{\mu_3\text{-SbFe}(\text{CO})_4\}]^-$ (**13**).^[21] Both of these clusters contain an iron triangle capped by a $\mu_3\text{-SbFe}(\text{CO})_4$ moiety. The structures of (**12**) and (**13**) are almost identical except that (**13**) has one more bridging hydride ligand. The average antimony-iron bond lengths within the SbFe_3 tetrahedron (246.7(7) pm for (**12**) and 247.9(8) pm for (**13**)) for both clusters are shorter than the antimony-iron bond distances to the terminal $\text{Fe}(\text{CO})_4$ groups of 252.1(2) pm for (**12**) and 250.73(8) pm for (**13**). This difference, however, is not so apparent in other similar clusters such as $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-SbFe}(\text{CO})_4\}_2]^{2-}$ and $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})\{\mu_3\text{-SbFe}(\text{CO})_4\}]^-$ whose bond lengths are discussed below. Indeed in the latter case, be it to a lesser extent, the exact opposite is true. The iron-iron bond lengths in both (**12**) and (**13**) are normal. The slightly longer iron-iron bond distances (one for cluster (**12**) and two for cluster (**13**)) indicate the positions of the bridging hydride ligands. The presence and nature of the hydride ligands are

supported by ^1H nmr data and the positioning of the surrounding carbonyl ligands.

The cluster $[\text{Fe}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-SbFe}(\text{CO})_4)]^-$ (**14**), which is produced in the reaction between antimony trichloride and $[\text{Et}_4\text{N}]_2[\text{Fe}_4(\text{CO})_{13}]^{[22]}$ is structurally similar to (**12**) in that the bridging hydride is replaced by a bridging carbonyl ligand. The metal-metal bond lengths in (**14**) are essentially the same as the corresponding bond lengths found in the isoelectronic hydride (**12**). The related cluster $[(\text{C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{SbFe}_3(\text{CO})_9\text{CH}]$ (**3b**), identified by spectroscopic means, is produced when $[(\mu_3\text{-Sb})\text{Fe}_3(\text{CO})_9(\mu_3\text{-CH})]$ is treated with $[(\text{C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{THF}]^{[5]}$ (**3b**) is thought to be isostructural with the arsenic analogue (**3a**) discussed earlier.

Oxidation of the previously mentioned complex (**11a**) with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ in acetonitrile leads to the formation of $[\text{Fe}_2(\text{CO})_8(\mu\text{-Sb}\{\text{Fe}(\text{CO})_4\}_2)]^-$ (**15**), which consists of an $\text{Fe}_2(\text{CO})_8$ moiety bridged by an $\text{Sb}\{\text{Fe}(\text{CO})_4\}_2$ group.^[23] Thus the central antimony atom is surrounded by a distorted tetrahedron of iron atoms, two of which belong to two terminal $\text{Fe}(\text{CO})_4$ groups with an average antimony-iron bond distance of 257.0(3) pm. The antimony-iron (263.7(8)_{av} pm) and iron-iron (272.0(1) pm) bond distances in the Sb_2Fe triangle are normal. (**15**) cannot, however, be considered as a simple substitution product of $\text{Fe}_2(\text{CO})_9$ as there are no carbonyls bridging the iron-iron bond. There is no apparent reason for this lack of bridging carbonyls; the more highly charged lead analogue, $[\text{Fe}_2(\text{CO})_8(\mu\text{-Pb}\{\text{Fe}(\text{CO})_4\}_2)]^{3-}$ is a simple substitution product of $\text{Fe}_2(\text{CO})_9$ with one bridging carbonyl being replaced by a bridging $\text{Pb}[\text{Fe}(\text{CO})_4]_2^{3-}$ group.

The presence of the bridging carbonyls in the analogous isoelectronic heteronuclear complexes $[\text{Fe}_2(\text{CO})_8(\mu\text{-Sb}\{\text{Fe}(\text{CO})_4\}\{\text{Cr}(\text{CO})_5\})]^-$

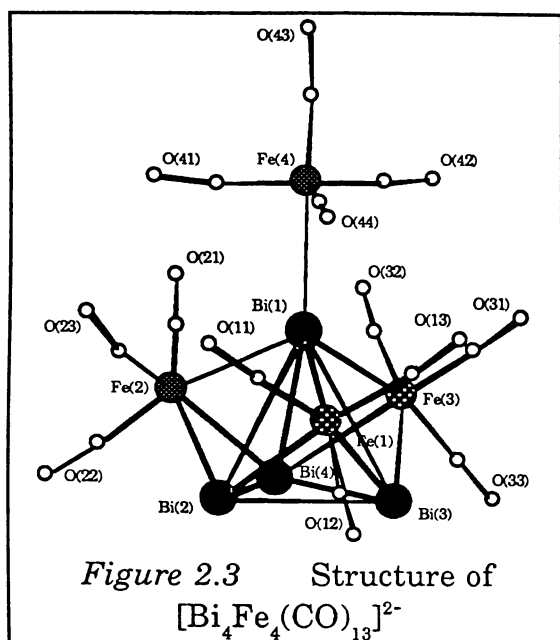
(E = Sb (**16a**), Bi (**16b**)), which are afforded from the reaction between what is thought to be $[\text{ECl}(\text{Fe}(\text{CO})_4)_3]^{2-}$ (E = Sb, Bi) and $[\text{Cr}(\text{CO})_5\text{THF}]$, is shown by the shorter iron-iron bond lengths of ~260 pm found for both clusters. (**16a**) and (**16b**) are structurally similar to (**15**), with the only difference being that one of the terminal $\text{Fe}(\text{CO})_4$ moieties on the bridging group fifteen atom of (**15**) is replaced by a $\text{Cr}(\text{CO})_5$ moiety. The metal-metal bond lengths found in (**16a**) are similar to those found in (**15**), with those found in (**16b**) exhibiting the expected increase in length due to the larger size of the bismuth atom as compared to antimony.

Oxidation of the antimony analogue (**16a**) produces the *spiro*-complex $[\text{Fe}_2(\text{CO})_6\{\mu\text{-Sb}(\text{Fe}_2(\text{CO})_8)\}_2]$ (**17**), whereas for the bismuth analogue (**16b**) oxidation leads to the formation of the cluster $[(\mu_3\text{-Bi})_2\text{Fe}_3(\text{CO})_9]$ (**18**). The structures of these are discussed below. When refluxed in acetonitrile (**16a**) and (**16b**) also lead to different types of clusters, $[\text{Bi}_2\text{Fe}_4(\text{CO})_{13}]^{2-}$ (**19**) for the bismuth complex and $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-SbFe}(\text{CO})_4\}_2]^{2-}$ (**20**) for the antimony complex.^[24]

2.1.4 Iron Clusters Containing Multiple Antimony or Bismuth Atoms

2.1.4.1 Bismuth clusters

$[\text{Bi}_2\text{Fe}_2\text{Co}(\text{CO})_{10}]^-$ (**21**) and $[\text{Bi}_4\text{Fe}_4(\text{CO})_{13}]^{2-}$ (**22**) are the only complexes known of this type in which the group fifteen atoms are bonded to each other. The former is produced in the reaction between $[\text{Bi}_2\text{Fe}_3(\text{CO})_9]$ and $[\text{Co}(\text{CO})_4]^-$.^[25,26] The latter, which is obtained when the cluster $[\text{Et}_4\text{N}][\text{BiFe}_3(\text{CO})_9(\mu_3\text{-CO})]$ is treated at 500 psi with carbon monoxide in dichloromethane or as a minor product from the reaction between bismuth trichloride and $[\text{Bi}(\text{Fe}(\text{CO})_4)_4]^{3-}$ has a novel structure consisting of a tetrahedral Bi_4 core in which three faces are capped by $\text{Fe}(\text{CO})_3$ moieties and the apical bismuth atom is bonded to an $\text{Fe}(\text{CO})_4$ group. Bi-Bi distances around the remaining bare face (315.7_{av} pm) are markedly



shorter than the Bi-Bi distances involving the apical bismuth atom in the Bi_4 tetrahedral core (346.6_{av} pm). Conversely the $\text{Bi}(1)\text{-Fe}_{\text{cluster}}$ bond lengths (270.3_{av} pm) are shorter than the other $\text{Bi-Fe}_{\text{cluster}}$ bond lengths (ranging from $271.4(6)$ to $275.3(6)$ pm). The $\text{Bi}(1)\text{-Fe}_{\text{terminal}}$ bond length of $275.2(6)$ pm is one of the longest bismuth-iron interactions in the dianion. It is comparable to similar interactions in other

complexes.^[27,28] The two Bi-Bi distances observed for (22) are comparable with the shortest distances in the pure element (307 and 353 pm).^[29] Comparison with the Bi_4^{2-} dianion shows that the Bi-Bi distances are considerably longer in (22), possibly due to π -interactions in the square-planer, 6π -electron Bi_4^{2-} system.^[30]

The heteronuclear anionic cluster (21) consists of a tetrahedral Bi_2Fe_2 core with a $\text{Co}(\text{CO})_4$ moiety bridging the Bi-Bi edge. The Bi_2Fe_2 framework possesses five skeletal pairs of electrons, whereas there should be six for tetrahedral bonding. The additional pair of electrons is probably provided by the $\text{Co}(\text{CO})_4^-$ bridge. This Bi-Bi bond length of $309.2(2)$ pm is short, but it remains within the range of known single bond lengths.^[31] The Bi-Fe bond distances of $266.9(5)$ to $269.3(5)$ pm are normal, while the Bi-Co bond distances of $286.8(5)$ and $289.4(5)$ pm are longer than one would expect for a bismuth-cobalt bond.^[17]

Also isolated from the above reaction is the complex (19), which can be obtained from either the reaction between bismuth trichloride and $[\text{Bi}\{\text{Fe}(\text{CO})_4\}_4]^{3-}$ in acetonitrile or the reaction between $[\text{Fe}(\text{CO})_4]^{2-}$ and

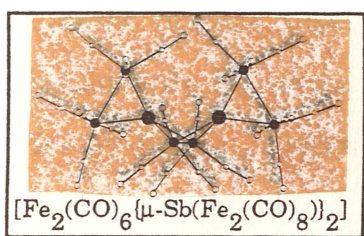
$[\text{Bi}_2\text{Fe}_3(\text{CO})_9]$ in tetrahydrofuran.^[26] The structure of the bimetallic dianion (19) is based upon a square-pyramidal Bi_2Fe_3 core (the bismuth atoms are positioned *trans* across the square base) with a terminal $\text{Fe}(\text{CO})_4$ moiety bonded to one of the bismuth atoms. Thus one of the bismuth atoms, Bi(1), is four-coordinate and the other, Bi(2), is three-coordinate. Each of the core iron atoms is bonded to three terminal carbonyl ligands. The Fe-Bi(2) bond lengths are longest at 268.3 ± 0.5 pm, with the Bi(1) to terminal iron bond length being slightly shorter at 266.8(2) pm. The Bi(1)-Fe core bond lengths, as well as being the shortest, show a marked variation. Bond distances between Bi(1) and the basal iron atoms are 259.5(2)_{av} pm, with the bond distance to the apical, seven-coordinate iron atom 5 pm longer at 264.5(2) pm. Iron-iron bond lengths of 279.6(2) and 280.8(2) pm are normal and the Bi...Bi distance of 339.8(2) pm is regarded formally as non-bonding.^[25]

The two complexes $[\text{Bi}_2\text{Fe}_3(\text{CO})_9]^{2-}$ are obtained from the sequential one-electron reduction of $[\text{Bi}_2\text{Fe}_3(\text{CO})_9]$ (18) in tetrahydrofuran or by reduction with cobaltocene in either benzene or dichloromethane respectively.^[26] Spectroscopic studies suggest that both of these anionic clusters have a structure similar to the core arrangement found in (19). However no structural data have been presented.

(18) is one of the products isolated from the reaction between sodium bismuthate and $[\text{HFe}(\text{CO})_4]^-$ followed by protonation with sulphuric acid.^[32] The above cluster, which lies on a site of crystallographic C_{2v} symmetry, has a trigonal bipyramidal Bi_2Fe_3 core with the two bismuth atoms occupying the apical sites. The equatorial iron atoms, which are each linked to three terminal carbonyl ligands, are disordered with the two Fe_3 triangles displaced by $\sim 30^\circ$. This disordering, however, seems to have no effect on the positions of the oxygen atoms, which are ordered. The order of the carbon atoms is somewhat intermediate, with

only three pairs of “half-carbon” atoms resolved. Any disorder, if present, in the remaining carbon atoms could not be resolved. Considering one discrete $(\mu_3\text{-Bi})_2\text{Fe}_3(\text{CO})_9$ molecule, the iron-iron bond lengths (ranging from 272.4(2) to 275.7(5) pm) are significantly longer than those found in clusters (**1c,6,7**), where one of the bridging bismuth atoms is replaced by a bridging CR group, and in (**4**), in which the bismuth atoms are replaced by arsenic atoms. This is not surprising as the $\mu_3\text{-CR}$ and $\mu_3\text{-As}$ groups are sterically less demanding than the bulkier $\mu_3\text{-Bi}$ moiety. This substitution appears to have no effect on the bismuth-iron bond lengths. Bismuth-iron bond lengths in (**18**) (ranging from 261.7(2) to 264.3(2) pm) fall within the range found for the $\mu_3\text{-CR}$ clusters.

2.1.4.2 Antimony clusters



The number of multi-antimony-iron carbonyl clusters known is much less extensive. These include $[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-SbFe}(\text{CO})_4\}_2]^{2-}$ (**23**),^[22] which is produced in the reaction between sodium antimonate and methanolic iron pentacarbonyl, and $[\text{Fe}_2(\text{CO})_6\{\mu\text{-Sb}(\text{Fe}_2(\text{CO})_8)\}_2]$ (**24b**),^[33,34] which has been reported by two groups, prepared by different routes although both involved salt elimination reactions between $[\text{Fe}_2(\text{CO})_8]^{2-}$ and antimony trichloride. Both groups characterised (**24b**) by single crystal X-ray crystallography, each isolating different isomorphs. Whitmire *et al* obtained red orthorhombic crystals from dichloromethane and Cowley *et al* report green monoclinic crystals from hexane. (**24b**) consists of an $[\text{Fe}(\text{CO})_3]_2$ group bridged by two $\{\text{Sb}[\text{Fe}(\text{CO})_4]_2\}$ moieties. The core bond lengths in both isomorphs of (**24b**) are essentially the same. The iron-iron bond lengths are all approximately 284 pm with the central, shared iron-iron bond being marginally longer than the outer ones in both clusters. The antimony-iron bond lengths in both clusters can be divided into two groups with the bond distances

between the antimony atoms and the outer iron atoms being the longer at approximately 255 pm. The antimony-iron bond distances involving the inner iron atoms are shorter at ~250 pm.

The pseudooctahedral cluster $[\text{Fe}_4(\text{CO})_{12}\{\mu_4\text{-SbFe}(\text{CO})_4\}_2]^{2-}$ (25), which has the $\{\mu_4\text{-SbFe}(\text{CO})_4\}$ groups *trans* to each other, can be obtained by either photolysis of the previously discussed $[\text{Fe}_2(\text{CO})_8(\mu\text{-Sb}\{\text{Fe}(\text{CO})_4\}_2)]$; with UV light or from the reaction of antimony trichloride with $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ ^[23] (25) has a core geometry the same as a variety of other main group-transition metal clusters.^[35] The antimony-iron bond lengths fall into two categories with each iron atom having one long and one short bond to antimony. The result of this is a puckered Fe_4 square, as found in other eight skeletal electron pair clusters of this type (according to the Wade/Mingos formalism there should only be seven skeletal electron pairs for an octahedral cluster). The Sb- $\text{Fe}_{\text{terminal}}$ distances (both 253.8(2) pm) are normal. The Fe-Fe bond lengths are long at 283.2(2)_{av} pm. These long bond lengths can be rationalised in terms of the extra pair of skeletal electrons. It has been shown^[36] that the eighth pair of electrons, in clusters of this type, occupies a low lying antibonding π^* orbital which is primarily localised on the four transition metals of the octahedron. Population of this antibonding orbital should thus lengthen the iron-iron bond lengths.

2.1.5 Previous Work with Group Fifteen Hydrides

The above preparations involve ionic reactants. There has been little work undertaken^[2,3] reacting reagents like AsH_3 , MeAsH_2 and SbH_3 with the neutral metal carbonyls.

The reaction of arsane with $[\text{Co}_2(\text{CO})_8]$ leads to the formation of the trimer $[\mu_4\text{-AsCo}_3(\text{CO})_8]_3$. The reaction is thought initially to parallel the reaction between monophenylgermane and $[\text{Co}_2(\text{CO})_8]$, in which $[(\text{OC})_4\text{Co}(\text{Ph})\text{GeCo}_2(\text{CO})_7]$ is formed followed by conversion with

decarbonylation to $[\text{PhGeCo}_3(\text{CO})_9]$ on heating.^[37] The analogous arsenic compound, $[\text{AsCo}_3(\text{CO})_9]$, is not isolated due to the Lewis-base site on the arsenic atom displacing a carbonyl ligand on another $[\text{AsCo}_3(\text{CO})_9]$ molecule such that the cyclic trimer is formed.

The reaction of monomethylarsane with $[\text{Co}_2(\text{CO})_8]$, however, did not parallel the dimethylgermane case, where dimethylgermane reacts with $[\text{Co}_2(\text{CO})_8]$ to give two derivatives of $[\text{Co}_2(\text{CO})_8]$.^[38]

Similarly the reactions of arsane and monomethylarsane with $[\text{Ge}(\text{Co}_2(\text{CO})_7)_2]$ did not parallel the analogous reactions involving the isoelectronic monomethylgermane and dimethylgermane. There was, respectively, little or no participation of the arsenic containing species, whereas carbonyl substitution was observed for the germanium species.^[2,39]

2.1.6 Products from the Reaction of Germanes and Stannanes with Iron Carbonyls.

Comparison of the energy of the arsenic-hydrogen bonds in arsane molecules and germanium-hydrogen bonds in germane molecules show that these bonds are of similar strength (see Table 2.2). If the lone pair on the arsenic atom is considered as a methyl group then the reactivities of germanes and arsanes would be expected to be similar. This somewhat strained analogy provided the impetus for the work reported in this chapter.

The reaction of MeGeH_3 with iron pentacarbonyl at temperatures above 130°C leads to the *spiro* cluster $(\mu_4\text{-Ge})[\text{Fe}_2(\text{CO})_8]_2$ (**26a**) and the trigonal bipyramidal cluster $(\mu_3\text{-GeMe})_2\text{Fe}_3(\text{CO})_9$ (**27**).^[40] In the analogous reaction using GeH_4 the same *spiro* cluster was obtained, but no equivalent $(\mu_3\text{-GeH})$ cluster was isolated.^[40]

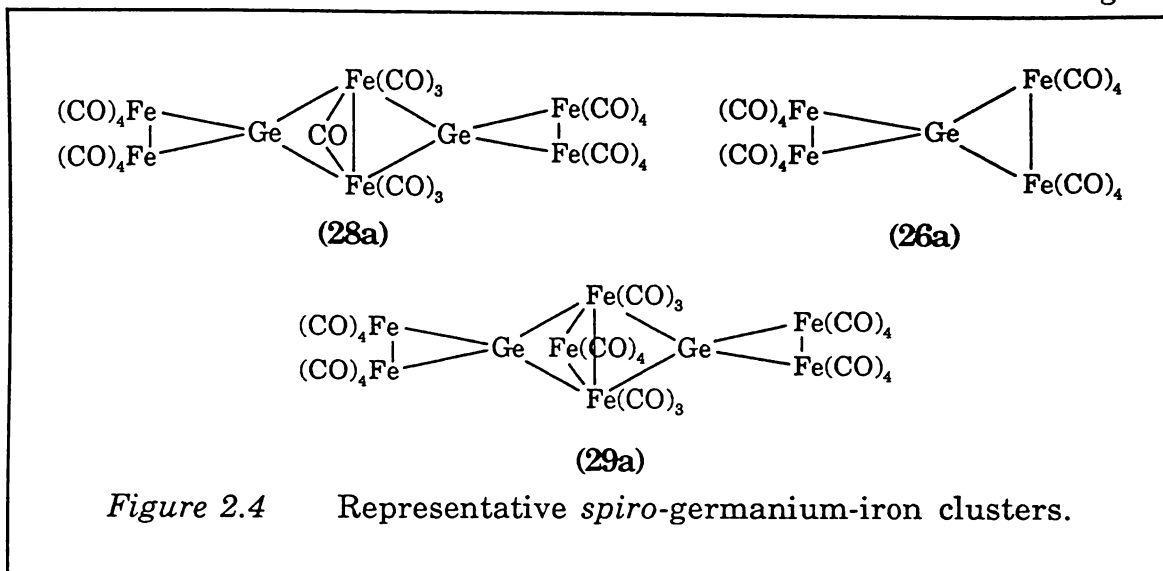
Table 2.2 Bond energies of group 14 and group 15 hydrides (kJ mol⁻¹).

C-H	416	N-H	391
Si-H	323	P-H	322
Ge-H	290	As-H	247
Sn-H	252	Sb-H	255

The open tube reaction at 68°C between GeH₄ and Fe₂(CO)₉ leads to the *spiro* clusters (μ₄-Ge)[Fe₂(CO)₈]₂, [Fe₂(CO)₈(μ₄-Ge)]₂[Fe₂(CO)₇] (**28a**) and [Fe₂(CO)₈(μ₄-Ge)]₂[Fe₃(CO)₁₀] (**29a**),^[41,42] with the first cluster being the major product. All these products can be explained in terms of a GeH₂ moiety substituting for a carbonyl bridging an iron-iron bond with the release of H₂ and CO. The very small quantities of (**29a**) probably result from reaction with Fe₃(CO)₁₂ which forms in the reaction mixture. Analogous products, (**26b**, **28b**, **29b**), were obtained when the above reaction was attempted using SnH₄ in place of the monogermane, with the mono-substituted Fe₃(CO)₁₂ derivative [Fe₂(CO)₈(μ₄-Sn)][Fe₃(CO)₁₁] (**30**) also being isolated.^[43,42]

In the reaction between MeSnH₃ and Fe₂(CO)₉ the MeSnH₃ is thought to disubstitute the Fe₂(CO)₉. This breaks the iron-iron bond to yield [MeSnHFe(CO)₄]₂ (**31b**).^[44] The analogous product, (**31a**), was obtained when the above reaction was attempted using MeGeH₃ in place of the MeSnH₃. Also isolated was (μ₂-GeMeH)₂Fe₂(CO)₇ (**32**) in which the iron-iron bond is retained and an extra carbonyl is lost.^[40]

The major products obtained from the reaction between MeGeH₃ and triiron dodecacarbonyl did not retain the triiron triangle. These were (**32**) and (μ₂-GeMeH)₃Fe₂(CO)₆ (**33**); both can be considered to be Fe₂(CO)₉ derivatives. The other product isolated was (**27**) which consists of a triiron triangle capped on both sides by a GeMe moiety.^[40]



It should be noted that reactions between monogermanes and $\text{Co}_2(\text{CO})_8$ lead to similar products such as $[(\mu_4\text{-Ge})\{\text{Co}_2(\text{CO})_7\}_2]$, $[\text{Co}_2(\text{CO})_7(\mu_4\text{-Ge})]_2[\text{Co}_2(\text{CO})_6]$, $[\{(\text{CO})_7\text{Co}_2(\mu_4\text{-Ge})\text{Co}_2(\text{CO})_6\}_2(\mu_4\text{-Ge})]$,^[45] $[(\text{OC})_4\text{Co}(\text{Me})\text{ECO}_2(\text{CO})_7]$ ($\text{E} = \text{Si}$,^[46] Ge ^[47]), $[(\text{Me}_2\text{Ge})\text{Co}_2(\text{CO})_7]$ and $[(\text{Me}_2\text{Ge})_2\text{Co}_2(\text{CO})_6]$.^[48]

2.2 REACTION OF ARSANE WITH IRON PENTACARBONYL

2.2.1 Experimental

All reactions of arsane with $\text{Fe}(\text{CO})_5$ were carried out in an ampoule as described in Chapter One. Arsane was produced as described in Chapter One. Reactions at temperatures over 70°C were attempted with the ampoule in a steel pressure vessel using $100\text{--}130^\circ\text{C}$ petroleum spirit as the solvent whereas at other temperatures $60\text{--}80^\circ\text{C}$ petroleum spirit was used. The quantities and conditions for all the runs are summarised in Table 2.3. A typical run is described below:

Arsane (0.5 mmol) and $\text{Fe}(\text{CO})_5$ (2 ml, 2.14 g, 14.8 mmol) in $100\text{--}130^\circ\text{C}$ petroleum spirit (5 ml) were sealed in an ampoule as described in Chapter One. The ampoule was then placed inside a bomb and heated at 110°C for 30 min. After this time the ampoule containing a red-brown mixture was removed and allowed to cool to room temperature. The

Table 2.3 Reaction quantities and conditions for the reactions of arsane with $\text{Fe}(\text{CO})_5$.					
Run	Arsane mmol	$\text{Fe}(\text{CO})_5$ mmol	Volume of solvent used ml	Temperature °C	Reaction time min
1	0.5	14.8	8	155	60
2	0.5	14.8	5	110	30
3	0.5	14.8	5	70 & 94	120 & 1200
4	0.5	14.8	5	94	300
5	0.5	14.8	5	110	1200
6	0.5	14.8	5	120	180
7	2.5	14.8	5	125	240

ampoule was opened as described in Chapter One. The incondensable gases were discarded.

The volatile fraction contained the solvent, $\text{Fe}(\text{CO})_5$ and some unreacted arsane, identified by infrared spectra.

The hexane-soluble fraction was passed through an alumina column (2 x 5 cm, activity III) eluting with dichloromethane until the eluent was colourless. This gave a wine red solution from which the dichloromethane was removed under vacuum to yield bis(μ_3 -arsino)nona-carbonyltriiron ($3\text{Fe}-\text{Fe}$) (0.0218 g, 15%) $\nu(\text{CO})_{\text{hexane}}$ (2037 vs and 2006 m) cm^{-1} .

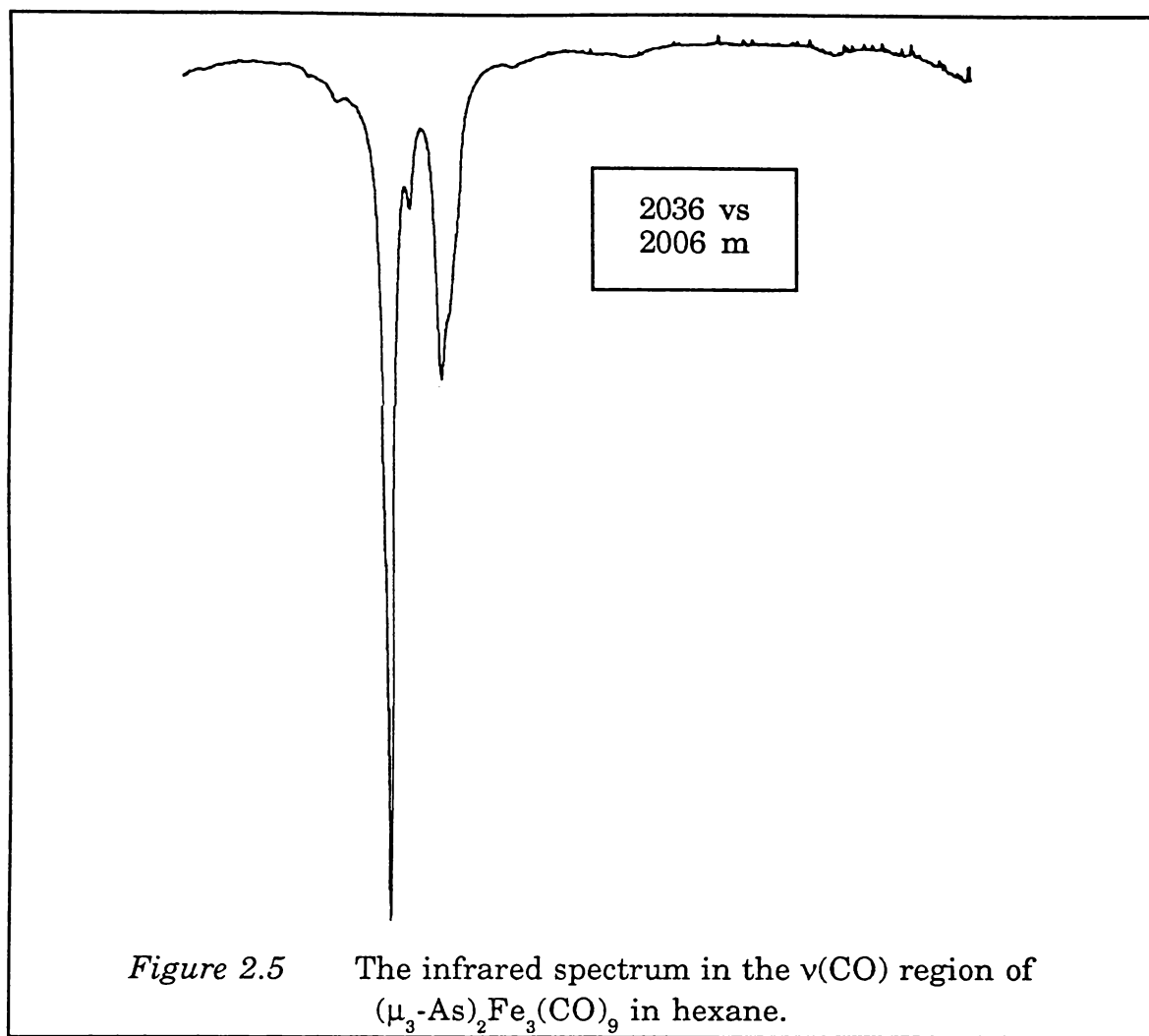
The remaining solid was extracted into dichloromethane. After the solvent was removed under vacuum the residue was washed with hexane (5 ml). This was repeated until the hexane washings were free of (μ_3 -As) $_2\text{Fe}_3(\text{CO})_9$. A brown solid remained (0.0213 g) $\nu(\text{CO})_{\text{dichloromethane}}$ (2080 m, 2064 vs and 2017 w) cm^{-1} .

The black solid which remained after the dichloromethane extraction was slightly soluble in THF and acetone, $\nu(\text{CO})_{\text{THF}}$ (2052 w, 2033 w and 1959 w) cm^{-1} .

2.2.2 Results

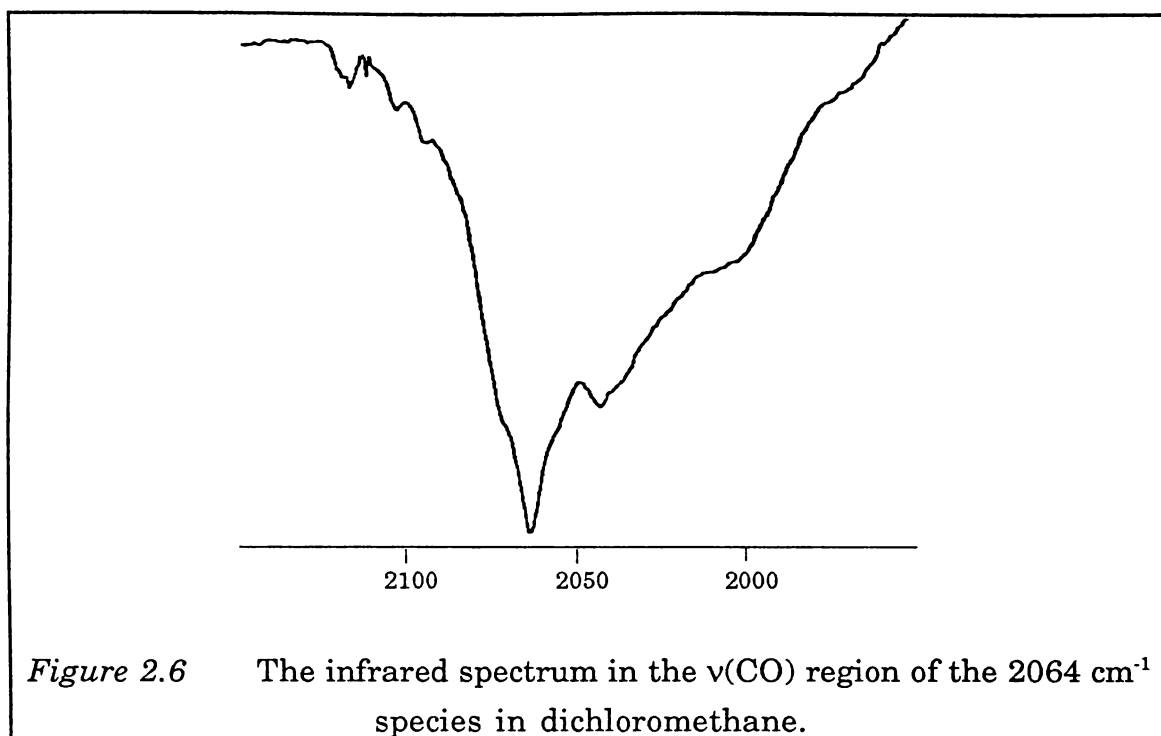
The reaction between arsane and $\text{Fe}(\text{CO})_5$ was attempted at various temperatures, ranging from 70 to 150°C, and reaction times as shown in Table 2.3. The only identifiable product obtained from these reactions was $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$, identified by its infrared spectrum^[9] (see Figure 2.5), with the best purified yield of 20% being obtained in run 2, which had a temperature of 110°C and a reaction time of 30 minutes. Although the yield of $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$ was only moderate, it is a hundred-fold improvement on 0.2%, the yield obtained in the only previously reported route.^[9] At all other reaction temperatures the yield of $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$ was lower with little or none produced at temperatures below 100°C or above 130°C as shown in Table 2.4. Below 100°C the reaction was much slower: no reaction occurred at 70°C, and at 94°C even after 5 hours little reaction had taken place with no $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$ being formed. Above 130°C there was a marked increase in the amount of decomposition with a metallic mirror forming on the inside of the reaction vessel above the solvent level, indicating the decomposition of the gaseous arsane at these temperatures. Purification of $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$ was easily achieved by passing a hexane solution through a short alumina column

Table 2.4 Products obtained from the reactions of arsane with $\text{Fe}(\text{CO})_5$.					
Run	Yield of $\text{As}_2\text{Fe}_3(\text{CO})_9$ mmol	Yield of $\text{As}_2\text{Fe}_3(\text{CO})_9$ % ⁽¹⁾	Yield of 2064 cm^{-1} species. g	Arsane consumed %	Yield of $\text{As}_2\text{Fe}_3(\text{CO})_9$ % ⁽²⁾
1	-	-	-	-	-
2	0.038	15	0.021	75	20
3	>0	>0	>0	-	-
4	0.000	0	~0	-	-
5	0.032	13	>0	100	13
6	0.030	12	>0	-	-
7	0.145	12	>0	100	12
(1). Based on arsane added.					
(2). Based on arsane consumed.					

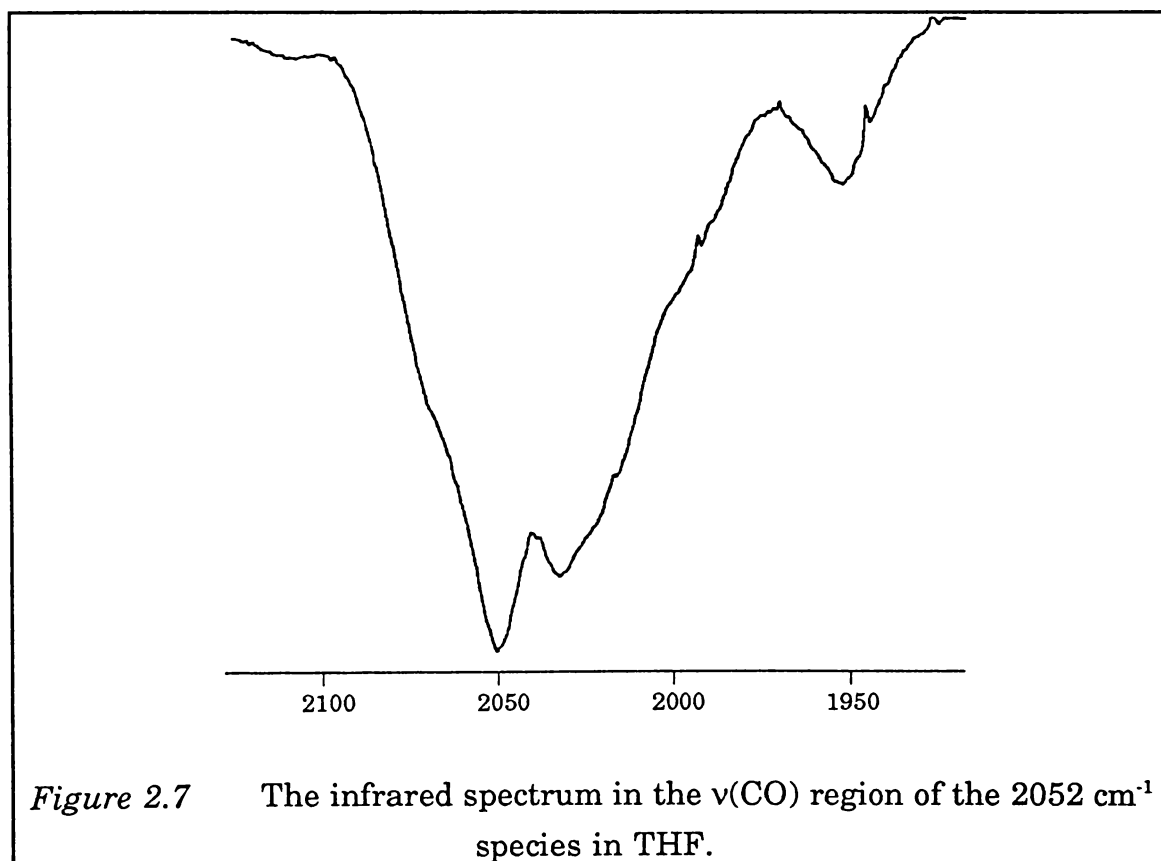


using petroleum spirit as the eluent. This gave a wine red solution from which the pure $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$ was isolated by removal of the solvent under vacuum. Highly pure red diamond-shaped crystals could be obtained from a saturated hexane solution held at -30°C for 3 days.

A second, as yet unidentified, species was isolated from the dichloromethane-soluble fraction in most runs. The infrared spectrum of this unknown species is shown in Figure 2.6, $\nu(\text{CO})_{\text{dichloromethane}}$ (2080 m, 2064 vs and 2017 w) cm^{-1} . This 2064 cm^{-1} species accounted for about one third of the involatile product mass. All attempts to crystallise the 2064 cm^{-1} species from cold dichloromethane, dichloromethane/hexane, dichloromethane/diethyl ether or diethyl ether solutions resulted in the



deposition of a fine dark brown powder. This powder upon warming to room temperature was no longer soluble in the solvent used, indicating decomposition.



The remaining black solid was very slightly soluble in either THF or acetone to give a faint brown solution with an infrared spectrum as shown in Figure 2.7, $\nu(\text{CO})_{\text{THF}}$ (2052 w, 2033 w and 1959 w) cm^{-1} . Infrared analysis of the condensable gases showed the presence of $\text{Fe}(\text{CO})_5$ in all cases, and the amount of arsane that had reacted was estimated by the intensity of its infrared bands in the gas phase.

2.3 REACTION OF ARSANE WITH DIIRON NONACARBONYL

2.3.1 Experimental

$\text{Fe}_2(\text{CO})_9$ (0.5 g, 1.37 mmol) and hexane (50 ml) were added to a round bottom flask (100 ml) fitted with a greaseless tap and the mixture was degassed. Into this was condensed arsane (1.0 mmol). The mixture was heated with occasional shaking at 70°C for 60 min. After this time the flask containing a red-brown solution and some unreacted $\text{Fe}_2(\text{CO})_9$ was removed from the heat and allowed to cool to room temperature. The flask was opened and worked-up as described in Chapter One. The incondensable gases were discarded.

The volatile fraction contained the solvent and $\text{Fe}(\text{CO})_5$, as identified by infrared spectra.

The hexane fraction showed the presence of minor amounts of $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$, identified by infrared spectroscopy, while the major green product (typically 75 - 100 mg) was obtained from this solution by cooling to -10°C. This compound was characterised as $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2\text{-}[\text{Fe}_2(\text{CO})_6]$ (**24a**) (15 - 20%) by a full X-ray crystal structure determination (see Section 2.5), $\nu(\text{CO})_{\text{dichloromethane}}$ (2114 w, 2097 s, 2066 s, 2058 w, 2044 vs, 1999 m and 1967 m) cm^{-1} (see Section 2.3.1.1), FAB mass spectrum m/e 1102 (M)⁺ and a succession of carbonyl fragment (m/e 28) losses down to m/e 654 ($M - 16\text{CO}$)⁺ (see Section 2.3.1.2).

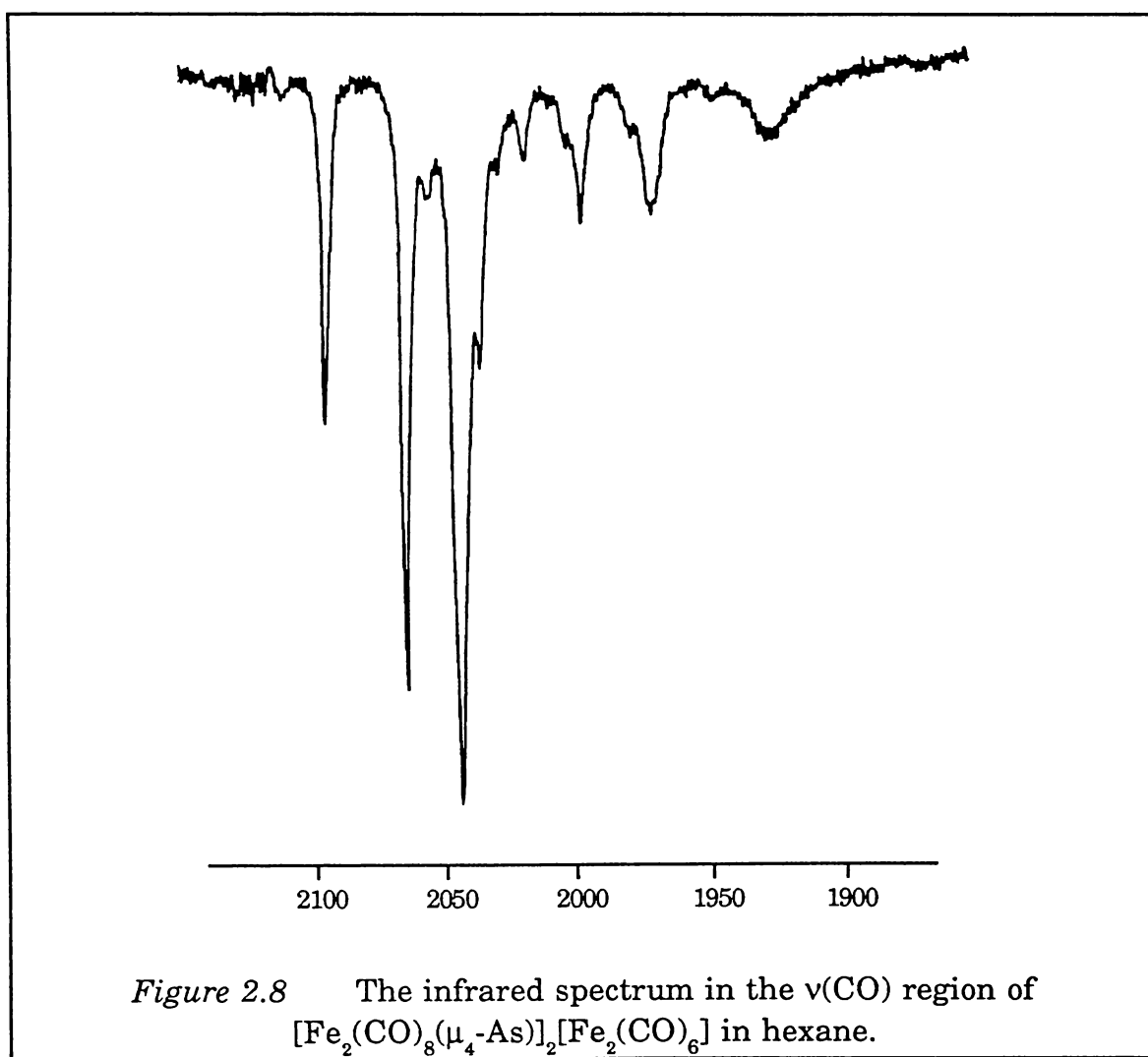
2.3.1.1 Vibrational Spectroscopy of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$

Infrared (hexane and dichloromethane) and Raman (dichloromethane) solution spectra for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ were recorded (Table 2.5 and Figure 2.8). It should be noted that the sample was decomposed in the laser beam and hence only weak Raman spectra were observed.

Table 2.5 Infrared and Raman Spectra of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-E})]_2[\text{Fe}_2(\text{CO})_6]$ (E = As, Sb, n = 6; E = Ge, n = 7).				
	E = As		E = Sb ^[33,34]	E = Ge ^[42]
Infrared	Infrared	Raman	Infrared	Infrared
hexane	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
2112 vw	2114 w	2104 w	2110 sh	-
2096 s	2097 s	-	2090 m	2090 m
2066 s	2066 s	-	2060 m	2054 vs
2059 w	2058 w	2059 vw	-	-
2046 vs	2044 vs	-	2038 s	2037 vs
2037 sh	-	-	-	-
2030 sh	-	-	-	-
2020 w	-	-	-	-
2004 sh	-	-	-	-
1998 m	1999 m	-	1995 w	1994 m
1982 sh	-	-	-	-
1973 m	1967 m	-	1960 w	1965 sh
1927 w	-	-	-	-
-	-	-	-	1827 vw
-	-	267 m	-	-

The highest symmetry possible for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ is D_{2h} , which gives an irreducible representation for the $\nu(\text{CO})$ modes of $5A_g + B_{1g} + 3B_{2g} + 2B_{3g} + A_u + 4B_{1u} + 3B_{2u} + 3B_{3u}$ (with the 10 B_u modes being infrared active and the 11 'g' modes being Raman active). Comparison with structures of similar compounds such as $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Sb})]_2[\text{Fe}_2(\text{CO})_6]$ suggests C_{2v} to be the highest expected symmetry in solution. This gives an irreducible representation for the carbonyl stretching modes of $8A_1 + 3A_2 + 7B_1 + 4B_2$. This predicts 20 infrared active modes (the A_1 , B_1

and B_2) and 23 Raman active modes (the A_1 , A_2 , B_1 and B_2). The observed spectra are much simpler than the predictions for C_{2v} with only thirteen bands observed in the hexane solution infrared spectrum, seven in the dichloromethane solution infrared spectrum and three in the dichloromethane solution Raman spectrum. The lower number of observed bands is attributable in the Raman case to the weak spectrum and in the infrared case probably to coincidental overlap of some fundamentals and low intensity of others. The thirteen bands observed in the hexane solution infrared excludes D_{2h} symmetry.



Comparison of the dichloromethane solution infrared spectrum, in the carbonyl stretching region, of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ with those of the isoelectronic $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Ge})]_2[\text{Fe}_2(\text{CO})_7]$ and the isomorphous

$[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Sb})]_2[\text{Fe}_2(\text{CO})_6]$ shows the spectra to be very similar; the only noticeable difference is a shift of $\sim 6\text{ cm}^{-1}$ to higher wave numbers for the arsenic cluster. The weak solution Raman spectrum of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ in dichloromethane shows only one band in the metal-metal region at 267 cm^{-1} as compared to 232 cm^{-1} the strongest band observed for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Ge})]_2[\text{Fe}_2(\text{CO})_7]$ in the same region. Given that the relative atomic masses for germanium and arsenic are similar, the higher energy vibration observed for the arsenic cluster may suggest that the As-Fe bond is stronger than the Ge-Fe bond for these clusters.

2.3.1.2 Mass Spectrum of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$

The FAB mass spectrum of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ was recorded. The highest envelope, centred at a m/e of 1098-1104, is assigned to $(M)^+$ (where $M = \text{As}_2\text{Fe}_6(\text{CO})_{22}$, the molecular ion). Envelopes corresponding to single carbonyl fragment ($m/e - 28$) losses down to m/e 654 ($M - 16\text{CO}$) $^+$ from this molecular ion were observed. Other prominent fragments are derived from the ion $(I)^+$ (where $I = \text{As}_2\text{Fe}_6\text{C}(\text{CO})_{17}$) with successive carbonyl fragment losses down to m/e 638 ($I - 12\text{CO}$) $^+$. The mass spectrum and assignments are given in Table 2.6.

Comparison of the ratio of intensities between the most intense and the second most intense peak in each of the envelopes indicates that Fe_6 fragments dominate in the higher mass envelopes (expected 2.63 : 1, found 2.5 : 1) and Fe_5 envelopes in the lower (expected 3.22 : 1, found 3 : 1). Ratios of intensities expected for the Fe_4 fragments of 5.55 : 1 were not observed.

2.3.2 Results

In the reactions of arsane with $\text{Fe}_2(\text{CO})_9$ the isolation of $\text{Fe}(\text{CO})_5$ in the product mixtures is understandable as the reactions were carried out at 70°C , which is near the temperature at which $\text{Fe}_2(\text{CO})_9$ decomposes thermally to give $\text{Fe}(\text{CO})_5$. The $\text{Fe}(\text{CO})_5$ present may have led to formation

Envelope	Int.	Assignment	Possible overlap fragments
1098 -1104	m	$\text{As}_2\text{Fe}_6(\text{CO})_{22}^+$	-
1070 -1076	vw	$\text{As}_2\text{Fe}_6(\text{CO})_{21}^+$	-
1042 -1048	vw	$\text{As}_2\text{Fe}_6(\text{CO})_{20}^+$	-
1014 -1020	vw	$\text{As}_2\text{Fe}_6(\text{CO})_{19}^+$	-
986 -992	vw	$\text{As}_2\text{Fe}_6(\text{CO})_{18}^+$	-
970 -976	vw	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{17}^+$	-
958 -964	vw	$\text{As}_2\text{Fe}_6(\text{CO})_{17}^+$	-
942 -948	vw	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{16}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{18}^+$
930 -936	m	$\text{As}_2\text{Fe}_6(\text{CO})_{16}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{18}^+$
914 -920	vw	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{15}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{17}^+$
902 -908	m	$\text{As}_2\text{Fe}_6(\text{CO})_{15}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{17}^+$
886 -892	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{14}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{16}^+$
874 -880	m	$\text{As}_2\text{Fe}_6(\text{CO})_{14}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{16}^+$
858 -864	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{13}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{15}^+$
846 -852	s	$\text{As}_2\text{Fe}_6(\text{CO})_{13}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{15}^+$
830 -836	vw	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{12}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{14}^+$
818 -824	s	$\text{As}_2\text{Fe}_6(\text{CO})_{12}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{14}^+$
802 -808	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{11}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{13}^+$
790 -796	s	$\text{As}_2\text{Fe}_6(\text{CO})_{11}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{13}^+$
774 -780	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_{10}^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{12}^+$ $\text{As}_2\text{Fe}_4\text{C}(\text{CO})_{14}^+$
762 -768	vs	$\text{As}_2\text{Fe}_6(\text{CO})_{10}^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{12}^+$ $\text{As}_2\text{Fe}_4(\text{CO})_{14}^+$
746 -752	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_9^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{11}^+$ $\text{As}_2\text{Fe}_4\text{C}(\text{CO})_{13}^+$
734 -740	m	$\text{As}_2\text{Fe}_6(\text{CO})_9^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{11}^+$ $\text{As}_2\text{Fe}_4(\text{CO})_{13}^+$
718 -724	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_8^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_{10}^+$ $\text{As}_2\text{Fe}_4\text{C}(\text{CO})_{12}^+$
706 -712	m	$\text{As}_2\text{Fe}_6(\text{CO})_8^+$	$\text{As}_2\text{Fe}_5(\text{CO})_{10}^+$ $\text{As}_2\text{Fe}_4(\text{CO})_{12}^+$
690 -696	m	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_7^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_9^+$ $\text{As}_2\text{Fe}_4\text{C}(\text{CO})_{11}^+$
678 -684	m	$\text{As}_2\text{Fe}_6(\text{CO})_7^+$	$\text{As}_2\text{Fe}_5(\text{CO})_9^+$ $\text{As}_2\text{Fe}_4(\text{CO})_{11}^+$
662 -668	w	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_6^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_8^+$ $\text{As}_2\text{Fe}_4\text{C}(\text{CO})_{10}^+$
650 -656	m	$\text{As}_2\text{Fe}_6(\text{CO})_6^+$	$\text{As}_2\text{Fe}_5(\text{CO})_8^+$ $\text{As}_2\text{Fe}_4(\text{CO})_{10}^+$
634 -640	m	$\text{As}_2\text{Fe}_6\text{C}(\text{CO})_5^+$	$\text{As}_2\text{Fe}_5\text{C}(\text{CO})_7^+$ $\text{As}_2\text{Fe}_4\text{C}(\text{CO})_9^+$

of the small amount of $(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9$ found in the product mixtures.

The major soluble product, typically isolated in 15-20% yields, was shown to be $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ by a FAB mass spectrum and a full X-ray single crystal structural study.

The antimony analogue of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ has been previously prepared by two independent groups^[33,34] by salt elimination reactions involving SbCl_3 . $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Sb})]_2[\text{Fe}_2(\text{CO})_6]$ was characterised by both groups by X-ray crystallography. Whitmire *et al* obtained red orthorhombic crystals from dichloromethane and Cowley *et al* obtained green monoclinic crystals from hexane. In this present work crystals of green $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ were isolated from hexane. However, they were isomorphous with the orthorhombic antimony complex.

2.4 $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$, AN X-RAY CRYSTALLOGRAPHIC STUDY

2.4.1 Data Collection

Needle shaped crystals were grown from a solution in hexane, which had been cooled to -10°C from room temperature. The crystals formed had a wide range of sizes with a high proportion of clustering and twinning. The larger crystals appeared black, with the very fine needles being green-black.

One of the few well-formed crystals was attached to a fine glass fibre with grease and mounted on a goniometer. Preliminary precession photography indicated orthorhombic symmetry with systematic absences appropriate for the Pbca space group.

The same crystal, of dimensions $0.34 \times 0.28 \times 0.12$ mm, was sent to the University of Canterbury for intensity data collection. Using a Nicolet P3 diffractometer with zirconium-filtered Mo-K_α radiation a total of 4529 unique reflections were collected within the range of $4^\circ < 2\theta < 52^\circ$. The resulting crystal data is given in Table 2.7.

Corrections were made for Lorentz and polarisation effects along with an empirical absorption correction which gave transmission factors

Table 2.7 Crystal data for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$

Molecular formula : $\text{As}_2\text{C}_{22}\text{Fe}_6\text{O}_{22}$

M = 1101.15

Crystal class : Orthorhombic

Space group : Pbca

a = 22.908(7) Å *U* = 6451(5)

b = 17.521(9) Å *Z* = 8

c = 16.071(7) Å *F*(000) = 4240

*D*_{calc} = 2.28 g cm⁻³

X-rays : Mo-K_α (λ = 0.710 73 Å)

Temperature of collection : -100°C

Linear absorption coefficient (μ) : 50 cm⁻¹

ranging from 0.663 to 0.572. This left 1322 reflections with $I > 2.5\sigma(I)$ which were used in all the calculations.

2.4.2 Solution and Refinement

The structure was solved using the TREF direct method routine of SHELXS86.^[49] This revealed all of the metal atoms. Subsequent refinement and difference-map cycles revealed all the carbonyl ligands. The iron and arsenic atoms were assigned anisotropic temperature factors in the final cycles, whereas the carbon and oxygen atoms were left isotropic. Atoms C(21), C(32), C(33) and O(23) would not refine satisfactorily until their temperature factors were fixed at reasonable values.

After introduction of a weighting scheme the refinement converged to give $R = 0.0995$ with $R_w = 0.0954$ and $w = (\sigma^2(F) + 0.003\ 06F^2)^{-1}$.

The thermal parameters of the atom centres were all of reasonable values, considering the quality of the data, as shown below.

Atom		As	Fe	C	O
U_{eq}/U_{11}	min	0.015	0.005	0.010	0.013
	max	0.018	0.018	0.130	0.100

The final difference map showed a few regions of electron density of ca. $1.55 e \text{ \AA}^{-3}$. This can be attributed to difficulties with absorption corrections and a weakly diffracting crystal. This is also shown by the higher than usual R factors. No parameter shifted by more than six percent of its estimated standard deviation in the final refinement cycle.

Table 2.8 Selected bond lengths and angles for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2\text{-}[\text{Fe}_2(\text{CO})_6]$

Bond Lengths (pm)

As(1)---Fe(1)	235(1)	As(2)---Fe(5)	241(1)
As(1)---Fe(2)	233.9(9)	As(2)---Fe(6)	239(1)
As(1)---Fe(3)	242(1)	Fe(1)---Fe(2)	268(1)
As(1)---Fe(4)	240.8(9)	Fe(5)---Fe(6)	272(1)
As(2)---Fe(1)	233(1)	Fe(3)---Fe(4)	275(1)
As(2)---Fe(2)	235(1)		

Bond Angles ($^\circ$)

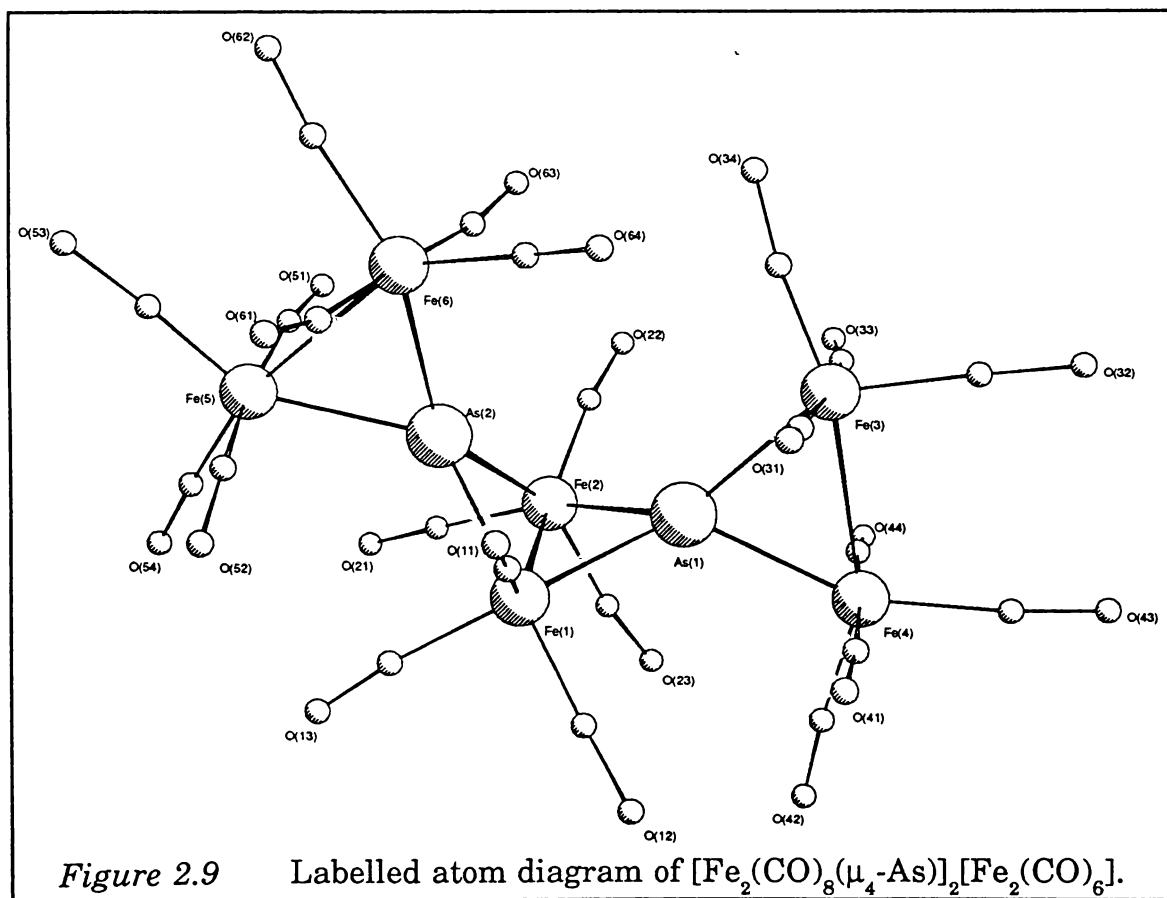
Fe(1)-As(1)-Fe(2)	69.9(3)	Fe(5)-As(2)-Fe(6)	69.2(3)
Fe(1)-As(1)-Fe(3)	140.2(4)	As(1)-Fe(1)-As(2)	84.4(3)
Fe(1)-As(1)-Fe(4)	126.0(4)	As(1)-Fe(1)-Fe(2)	54.9(3)
Fe(2)-As(1)-Fe(3)	133.3(4)	As(2)-Fe(1)-Fe(2)	55.4(3)
Fe(2)-As(1)-Fe(4)	129.0(4)	As(1)-Fe(2)-As(2)	84.1(3)
Fe(3)-As(1)-Fe(4)	69.5(3)	As(1)-Fe(2)-Fe(1)	55.2(3)
Fe(1)-As(2)-Fe(2)	70.0(3)	As(2)-Fe(2)-Fe(1)	54.6(3)
Fe(1)-As(2)-Fe(5)	128.5(4)	As(1)-Fe(3)-Fe(4)	55.1(3)
Fe(1)-As(2)-Fe(6)	132.7(4)	As(1)-Fe(4)-Fe(3)	55.4(3)
Fe(2)-As(2)-Fe(5)	127.9(4)	As(2)-Fe(5)-Fe(6)	55.2(3)
Fe(2)-As(2)-Fe(6)	139.8(4)	As(2)-Fe(6)-Fe(5)	55.6(3)

Selected bond lengths and angles are given in Table 2.8, while the remaining bond lengths and angles, the final positional parameters and final thermal parameters are listed in Appendix 2.

2.4.3 Discussion of the Structure of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$

The crystal structure of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ consists of discrete molecules. A labelled perspective of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ is shown in Figure 2.9 (labelled atom diagram).

The overall geometry of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ consists of four AsFe_2 triangles linked by common arsenic atoms and one iron-iron bond to give a structure derived from $\text{Fe}_2(\text{CO})_9$ with two of the bridging carbonyls replaced by two $[\mu\text{-AsFe}_2(\text{CO})_8]$ moieties. The iron atoms with two bridging arsenic groups attached each have three terminal carbonyls bonded to them and the other iron atoms each have four terminal carbonyls bonded. Each of the iron atoms is in a distorted octahedral environment, with all iron-iron and iron-arsenic linkages being *cis* with respect to each other. The structure of the antimony analogue, (24b), of (24a), as stated earlier, has been reported previously by two groups.^[33,34]



The crystals of (24a) were green and originated from hexane like the monoclinic antimony complex, but were isomorphous with the red orthorhombic antimony complex.

The iron-iron bond lengths are all essentially the same (268(1), 275(1) and 272(1) pm) with the central, shared iron-iron bond being marginally shorter than the outer ones. This is the opposite to what is observed for the analogous antimony clusters (24b), possibly due to the larger steric requirements of the two bulkier antimony groups. In contrast to this, the arsenic-iron bond lengths vary in the same way as found for the antimony clusters. The arsenic-iron bond distances can be divided into two groups with the bond distances between the arsenic atoms and the outer iron atoms being the longer (242(1), 240.8(9), 241(1) and 239(1) pm). The four arsenic-iron bond distances involving the inner iron atoms are shorter at 235(1), 233.9(9), 232(1) and 235(1) pm. This pattern was explained in terms of the *spiro* group fifteen atom contributing three bonding electrons to the inner diiron unit, and only two bonding electrons to the outer diiron groups. If electrons are counted as above the electron count at each iron atom is 18. This interpretation is further supported by comparison with some of the pseudo-isostructural and isoelectronic group fourteen compounds.

A wide variation in dihedral angles between the EM_2 triangles in 102-electron, linked-triangle E_2M_6 compounds can be found (see Table 2.9). The dihedral angles between the $AsFe_2$ triangles in (24a) (at 84.7 and 86.1° in the *spiro* cases and 109.9° for the butterfly angle) are very close to those found for the antimony analogue (24b). However, when compared to the germanium cluster (28a), (a very wide butterfly angle of 132.35° with *spiro*-dihedral angles almost perpendicular at 87.49 and 88.80°) or to the tin species (28b) (with one acute *spiro*-dihedral angle of 73.1° and a less deviant butterfly angle of 115.8°^[42]) and the mixed-metal

Table 2.9 Dihedral angles for selected E_2M_6 compounds ($^\circ$)

Compound		<i>spiro</i> -dihedral angles	butterfly angle
$[Fe_2(CO)_8(\mu_4-As)]_2[Fe_2(CO)_6]$	(24a)	84.7 86.1	109.9
$[Fe_2(CO)_8(\mu_4-Sb)]_2[Fe_2(CO)_6]$	(24b)		
$[Fe_2(CO)_8(\mu_4-Ge)]_2[Fe_2(CO)_7]$	(28a)	87.49 88.80	132.35
$[Fe_2(CO)_8(\mu_4-Sn)]_2[Fe_2(CO)_7]$	(28b)	73.1	115.8
$[Co_2(CO)_7(\mu_4-Ge)]_2[Fe_2(CO)_7]$	(34)	86.4 _{av}	111.0
$[Fe_2(\mu_2-GePh_2)_2(CO)_7]$			128.0
$[Fe_2(\mu_2-GeMe_2)_3(CO)_6]$			120.0
$[Fe_2(CO)_9]$			120.0
$(\mu_4-Ge)[Fe_2(CO)_8]_2$	(26a)	89.0	

cluster $[Fe_2\{(\mu_4-Ge)Co_2(CO)_7\}_2(CO)_7]$ (34) (butterfly angle of 111° and the average *spiro*-dihedral angle of $86.4^{o[50]}$) this variation is evident. The butterfly angles for the related complexes $[Fe_2(\mu_4-GePh_2)_2(CO)_7]$ (128°), $[Fe_2(\mu_2-GeMe_2)_3(CO)_6]$ (120°) and $[Fe_2(CO)_9]$ (120°) fall within this range as does the *spiro*-dihedral angle in (26a) (89°). The variety of angles, illustrating the flexibility of the metal core, arises from the minimisation of intra-molecular non-bonding interactions between oxygen atoms on the carbonyl ligands and from inter-molecular interactions imposed by the particular crystal lattices adopted.

In contrast to this are the related 102-electron clusters $[Fe_2\{(\mu_4-E)Co_2(CO)_7\}_8(CO)_8]^{2-}$ ($E = In^{[51]} \quad Tl^{[52]}$). Both of these clusters, which are situated about a centre of $2/m$ symmetry, have planer E_2Fe_2 central cores. The long central $Fe \cdots Fe$ (non-bonding) interactions of over 400 pm in these two clusters allow the butterfly angle to open out with a carbonyl ligand filling the extra site around the octahedral iron atoms.

The predicted symmetry of (24a) could be C_s , C_2 , C_{2v} or D_{2h} . If the structure observed in the crystalline state is maintained in solution then the highest symmetry possible for (24a) in solution is C_s . If however some deviations are due to crystal packing and are negligible in solution then

the solution structure could be of higher symmetry. D_{2h} requires, among other constraints, the dihedral angle (the butterfly angle) at the central iron-iron bond to be 180° . In the crystal lattice an angle of 109.9° is found. This large deviation is not likely to be imposed by crystal packing forces, ruling out D_{2h} symmetry in solution, leaving C_2 and C_{2v} as the other possible solution symmetries for (24a). This is in full agreement with the infrared data discussed in Section 2.3.1.1 which predicts C_{2v} to be highest possible solution symmetry for (24a). C_2 symmetry imposes the limitation that deviations in one side of the molecule must be matched on the other side of the molecule, the two fold axis bisecting the central iron-iron bond and the butterfly angle. To observe the two vertical planes required for C_{2v} symmetry the central iron-iron bond must be bridged symmetrically by the arsenic atoms and the dihedral angles between the $AsFe_2$ triangles at the *spiro* arsenic centres must be 90° (the outer $AsFe_2$ triangles do not have to be symmetrical, but any deviations must be the same in each end of the molecule).

2.5 REACTION OF ARSANE WITH TRIIRON DODECARBONYL AND ITS DERIVATIVES

2.5.1 AsH_3 with $Fe_3(CO)_{12}$

AsH_3 (2.0 mmol) and $Fe_3(CO)_{12}$ (0.317 g, 0.60 mmol) in pentane (7 ml) were sealed in an ampoule as described in Chapter One. The ampoule was then heated at $30^\circ C$ for 20 days to give a red-brown solution and a black solid. The ampoule was opened as described in Chapter One without freezing. The incondensable gases were quickly pumped away and the solution decanted into a Schlenk flask under nitrogen.

All attempts to analyse the red pentane soluble fraction were thwarted by decomposition to give $Fe_3(CO)_{12}$. Solutions decomposed in the solution cell within seconds, under nitrogen at room temperature within 2 hours and at $-20^\circ C$ overnight.

The black residue was insoluble in hexane and CH_2Cl_2 and was slightly soluble in THF to give a brown solution which decomposed rapidly in the solution cell.

2.5.2 AsH_3 with $\text{Fe}_3(\mu_3\text{-Bu}^t\text{NC})(\text{CO})_9$

2.5.2.1 Experimental

$[\text{Fe}_3(\mu_3\text{-}\eta^2\text{-CNBu}^t)(\text{CO})_9]$ (0.063 g, 0.13 mmol) was dissolved in 60-80°C petroleum spirit (20 ml) in a round bottom flask (100 ml) fitted with a greaseless tap. After degassing the solution, arsane (0.40 mmol) was condensed into the flask and the flask sealed. The mixture was left at 20°C for 72 hours and at 70°C for a further 24 hours, by which time there was formation of a black solid. The mixture was cooled to room temperature & worked-up as in Chapter One. The incondensable gases and volatile fractions were removed and discarded.

Dissolution of the residue with dichloromethane showed it to be unreacted $[\text{Fe}_3(\mu_3\text{-}\eta^2\text{-CNBu}^t)(\text{CO})_9]$ as identified by infrared spectroscopy.

2.5.2.2 Results

$[\text{Fe}_3(\mu_3\text{-}\eta^2\text{-CNBu}^t)(\text{CO})_9]$ has been found by Murray *et al* to react with many Lewis bases L to give $[\text{Fe}_3(\text{CNBu}^t)\text{L}_2(\text{CO})_9]$.^[53] Reactions were rapid and quantitative for L = CNBu^t , XyNC , P(OEt)_3 and PMe_2Ph giving rise to the corresponding mixed-ligand substituted clusters which were stable enough for characterisation. Reaction with PBu_3 and PPh_3 occurred more slowly and less specifically to give other substituted clusters. Other Lewis bases tried which did not react were AsPh_3 , dppe, dppm, thiophene and PhCCH . Results from this study concur with the above findings with the AsR_3 compound not reacting with $[\text{Fe}_3(\mu_3\text{-}\eta^2\text{-CNBu}^t)(\text{CO})_9]$ at moderate temperatures.

2.6 REACTION OF STIBANE WITH IRON CARBONYLS

The similar energies of the antimony-hydrogen and arsenic-hydrogen bonds (see Table 2.2) suggest that reactions involving the monostibanes with iron carbonyls may be a route to neutral antimony-iron clusters.

2.6.1 Reaction of Stibane with Iron Pentacarbonyl

All reactions of stibane with $\text{Fe}(\text{CO})_5$ were carried out in an ampoule as described in Chapter One using 100-130°C petroleum spirit as the solvent. Stibane was produced as per Section 1.4.2. Reactions at temperatures over 70°C were undertaken with the ampoule in a steel pressure vessel.

2.6.1.1 Experimental

Run 1 - Stibane (0.5 mmol) and $\text{Fe}(\text{CO})_5$ (2 ml, 2.14 g, 14.8 mmol) in 100-130°C petroleum spirit (5 ml) were sealed in an ampoule as described in Chapter One. The ampoule was placed inside a bomb and heated at 103°C for 30 minutes. The ampoule containing a black mixture was allowed to cool to room temperature. The ampoule was then opened as described in Chapter One. The incondensable gases were discarded.

The volatile fraction contained the solvent and $\text{Fe}(\text{CO})_5$, identified by infrared spectroscopy.

The pale yellow hexane fraction contained traces of a carbonyl-containing material, as shown to be $\text{Fe}(\text{CO})_5$ by infrared $\nu(\text{CO})_{\text{hexane}}$ (2023 w and 2000 w) cm^{-1} .

The remaining black solid (0.052 g) was insoluble in dichloromethane, THF and acetone.

Run 2 - Stibane (0.5 mmol) and $\text{Fe}(\text{CO})_5$ (2 ml, 2.14 g, 14.8 mmol) in 100-130°C petroleum spirit (5 ml) were sealed in an ampoule as

described in Chapter One. The ampoule was heated in an oil bath at 70°C for 48 hours, over which time the mixture turned black. The ampoule, after cooling to room temperature, was opened and the incondensable gases were discarded.

Infrared analysis of the volatile fraction showed it to contain the solvent and $\text{Fe}(\text{CO})_5$.

All attempts to dissolve the remaining black solid in dichloromethane, THF or acetone failed.

2.6.1.2 Results

Both the 70°C and the 103°C reactions of stibane with $\text{Fe}(\text{CO})_5$ resulted in the decomposition of the stibane to antimony metal, with an antimony mirror being formed on the inside of the ampoule, above the solvent level, in the higher temperature reaction. All the stibane had decomposed in both cases as apparent from the infrared spectra of the condensable volatiles. The black residue along with the antimony mirror in the 103°C reaction accounted for most of the antimony. The only difference between the two reactions was the length of time required to decompose all the stibane. At the higher temperature all the stibane had decomposed within 30 minutes, whereas at the lower temperature there was a small amount of decomposition after 5 hours, with full decomposition taking 48 hours.

2.6.2 Reaction of Stibane with Nonacarbonyl Diiron

2.6.2.1 Experimental

Stibane (1.0 mmol) and $\text{Fe}_2(\text{CO})_9$ (0.182 g, 0.5 mmol) in 100-130°C petroleum spirit (5 ml) were sealed in an ampoule. The ampoule was placed in an oil bath at 70°C for 24 hours. The ampoule, now containing a clear liquid and black solid, was removed and allowed to cool to room

temperature. The ampoule was opened and the incondensable gases were discarded.

The volatile fraction contained petroleum spirit and infrared analysis of the head space revealed a trace of $\text{Fe}(\text{CO})_5$.

The nonvolatile black residue was insoluble in hexane, dichloromethane and acetone.

2.6.2.2 Results

As with the reaction of stibane with $\text{Fe}(\text{CO})_5$, there were no tractable products obtained from the reaction of stibane with $\text{Fe}_2(\text{CO})_9$. The formation of small amounts of $\text{Fe}(\text{CO})_5$ during the reaction was through thermal decomposition of the $\text{Fe}_2(\text{CO})_9$. The flakes of $\text{Fe}_2(\text{CO})_9$ in the bottom of the reaction vessel slowly blackened as the reaction proceeded. This is probably a result of the stibane decomposing on the surface of the $\text{Fe}_2(\text{CO})_9$, explaining the absence of antimony in any of the other fractions isolated from the reaction mixture.

2.6.3 Reaction of Stibane with Dodecacarbonyl Triiron

2.6.3.1 Experimental

Stibane (1.04 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (0.210 g, 0.417 mmol) in 80-100°C petroleum spirit (7 ml) were sealed in an ampoule. The ampoule was heated in the dark at 49°C in an oil bath for 24 hours, at 70°C with shaking for 48 hours and at 70°C for 3 weeks. The ampoule was cooled to room temperature and opened. The incondensable gases were pumped away.

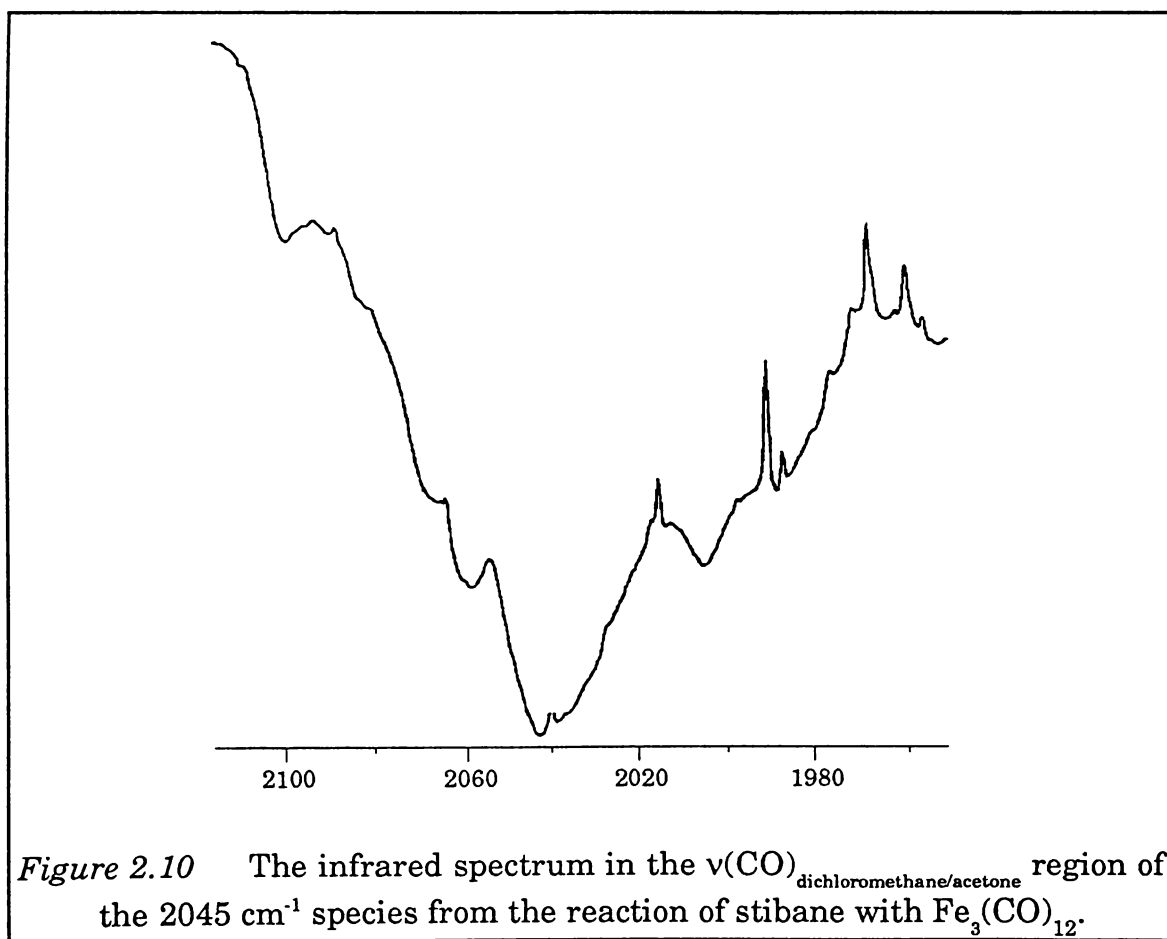
The clear volatile fraction consisted mainly of the solvent with a small amount of $\text{Fe}(\text{CO})_5$, evident from the 2022 cm^{-1} infrared band.

The remaining unidentified black solid was insoluble in hexane and dichloromethane and slightly soluble in acetone to give a spectrum as

shown in Figure 2.10, $\nu(\text{CO})_{\text{acetone}}$ (2102 w sh, 2060 w sh, 2045 m and 2006 w sh) cm^{-1} .

2.6.3.2 Results

As with the reactions of stibane with $\text{Fe}(\text{CO})_5$ and with $\text{Fe}_2(\text{CO})_9$, the reaction of stibane with $\text{Fe}_3(\text{CO})_{12}$ led to the formation of no tractable products. There was no apparent reaction after 24 hours in the dark at 49°C so the reaction temperature was increased to 70°C and the reaction continued for a further 48 hours. After the time the solution was still the green of $\text{Fe}_3(\text{CO})_{12}$, so the reaction was left to continue for a further 3 weeks. There was no stibane or $\text{Fe}_3(\text{CO})_{12}$ remaining at the end of the reaction as indicated by infrared. The $\text{Fe}(\text{CO})_5$ was produced by the thermal decomposition of $\text{Fe}_3(\text{CO})_{12}$.



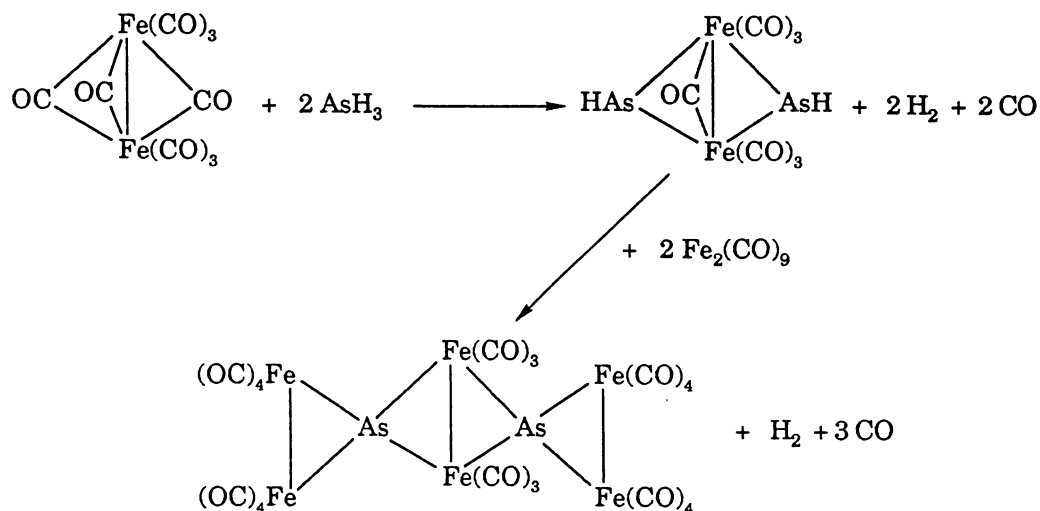
2.7 DISCUSSION OF THE REACTIONS BETWEEN GROUP 15 HYDRIDES AND IRON CARBONYLS.

In the reactions between the group 14 hydride, MeGeH_3 and $\text{Fe}(\text{CO})_5$, in hydrocarbon solvents, at elevated temperatures, the trigonal bipyramidal cluster $[(\mu_3\text{-MeGe})_2\text{Fe}_3(\text{CO})_9]^{[40]}$ is one of the products formed, the other being the *spiro* cluster $\{(\mu_4\text{-Ge})[\text{Fe}_2(\text{CO})_8]_2\}$ in which the germanium-carbon bond has been broken. Hence, the formation of $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ from the reaction of arsane with $\text{Fe}(\text{CO})_5$ was not unexpected. $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ was characterised by infrared analysis. The yields were not as good as those obtained for the germanium hydrides. However, the use of inexpensive starting materials coupled with the relatively straightforward preparative method means that workable quantities of pure $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ can now be prepared quickly and cheaply. In most of the reactions attempted between arsane and $\text{Fe}(\text{CO})_5$ a second, as yet unidentified, dichloromethane-soluble, product was isolated. The remaining two-thirds of the reaction mixture was essentially insoluble, black material which probably resulted from the decomposition of the reacting species. No evidence was attained for the formation of clusters analogous to the *spiro* cluster found in the germanium system. Such clusters would probably be ionic clusters of the type $[(\mu_4\text{-As})\{\text{Fe}_2(\text{CO})_8\}_2]^+$ or $[(\mu_4\text{-As})\{\text{Fe}_2(\text{CO})_8\}\{\text{Fe}_2(\text{CO})_7\}]^-$.

In an attempt to prepare the analogous antimony cluster $[(\mu_3\text{-Sb})_2\text{Fe}_3(\text{CO})_9]$, stibane was reacted with $\text{Fe}(\text{CO})_5$. However, the stibane decomposed to antimony metal at reaction temperatures greater than 70°C to give only traces of a soluble carbonyl-containing species. This is perhaps not surprising in view of the thermal instability of stibane.

The reaction of arsane with $\text{Fe}_2(\text{CO})_9$ follows the same reaction pathway as that seen for MeGeH_3 with $\text{Fe}_2(\text{CO})_9$. However the difference between the methyl group on the germane and the lone pair on the arsane

is then observed. This is in the form of loss of the remaining hydride on each arsenic atom with substitution across the iron-iron bond of an additional $\text{Fe}_2(\text{CO})_9$ molecule per arsenic atom. The postulated reaction pathways are given below:



$[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ was characterised by a full X-ray crystal structure determination. No direct evidence was obtained for the formation of $[(\mu_2\text{-AsH})_2\text{Fe}_2(\text{CO})_7]$. The similar germanium cluster, $[(\mu_2\text{-Ge}(\text{Me})\text{H})_2\text{Fe}_2(\text{CO})_7]$ can be isolated from the reaction between MeGeH_3 and $\text{Fe}_2(\text{CO})_9$. The germane reaction stops at this point, which would be expected as the methyl groups of $[(\mu_2\text{-Ge}(\text{Me})\text{H})_2\text{Fe}_2(\text{CO})_7]$ block the secondary substitution of further $\text{Fe}_2(\text{CO})_9$ molecules.

For each arsenic atom formation of the complex involves displacement of a carbonyl ligand from a neighbouring $\text{Fe}_2(\text{CO})_9$ molecule with loss of an hydrogen atom to give a *spiro* arrangement around the arsenic atom. Overall loss of one carbonyl ligand from the central $\text{Fe}_2(\text{CO})_7$ moiety occurs. There is no evidence from this experiment as to whether substitution and decarbonylation is stepwise or concerted.

Formation of cyclic products like those isolated from the reactions of MeGeH_3 and MeSnH_3 with $\text{Fe}_2(\text{CO})_9$, $[\text{MeE}(\text{H})\text{Fe}(\text{CO})_4]$ ($\text{E} = \text{Ge}, \text{Sn}$), in which the iron-iron bond has been broken was not evident.

The small amounts of $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ isolated from this reaction mixture are probably produced by reaction of arsane with the $\text{Fe}(\text{CO})_5$ obtained from the thermal degradation of the $\text{Fe}_2(\text{CO})_9$ starting material.

As for the $\text{Fe}(\text{CO})_5$ case, stibane was reacted with $\text{Fe}_2(\text{CO})_9$ to see if the antimony cluster analogous to the one obtained from the reaction of arsane with $\text{Fe}_2(\text{CO})_9$, $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$, could be obtained. The hydride decomposed at temperatures above 70°C , yielding no soluble carbonyl-containing species.

In conclusion the reactions reported above show that reactions of iron carbonyls with AsH_3 provide a practicable route to arsenic-containing iron clusters, although in only moderate yields. As found for reactions of the $\text{MeGeH}_3/\text{AsH}_3$ pair with $\text{Co}_2(\text{CO})_8$ there are some parallels between the reactions of AsH_3 and RGeH_3 with iron carbonyls. The formation of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ from AsH_3 and $\text{Fe}_2(\text{CO})_9$ is directly comparable to the production of $[\text{Co}_2(\text{CO})_7(\mu_4\text{-Ge})]_2[\text{Co}_2(\text{CO})_6]$ from GeH_4 and $\text{Co}_2(\text{CO})_8$ and to the production of $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-Ge})]_2[\text{Fe}_2(\text{CO})_7]$ from GeH_4 and $\text{Fe}_2(\text{CO})_9$.

However, in general the analogy of As-H with Ge-H has limited application but, not surprisingly, there are key differences. The major one being that with germanium a larger percentage yield of clusters is observed.

SbH_3 was too unstable with respect to decomposition for the formation of antimony-iron clusters by this route. A more promising route to the antimony analogue of $[(\mu_3\text{-As})_2\text{Fe}_3(\text{CO})_9]$ may be provided by modification of the three-step, non-hydride route used in the synthesis of the bismuth analogue $[(\mu_3\text{-Bi})_2\text{Fe}_3(\text{CO})_9]$.^[54]

There appears to be a need for a systematic study of the reactions of As-halides with anions.^[55] The work on Sb and Bi suggests there are many

species that should be available, and the reactions with anions may be more fruitful than the hydride routes.

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Chapter Three

CHAPTER THREE

REACTIONS OF ORTHO-ACYLATED PHENYLPHOSPHANES WITH METAL CARBONYLS

3.1 INTRODUCTION

Complexation of the substrate by transition metals plays an important role in catalytic processes. These processes require the formation of reactive intermediates, often formed by the facile elimination of a solvent molecule from labile solvent complexes.^[1,2] This gives a reactive intermediate with a vacant coordination site into which the substrate can be easily coordinated to undergo further reaction on the catalytically active metal. Generally the labile solvents contain oxygen functionalities in the form of ethers or ketones. The presence of tertiary phosphanes in the coordination sphere of the catalytic transition metal can often influence the selectivity of the reaction towards a particular product.^[3]

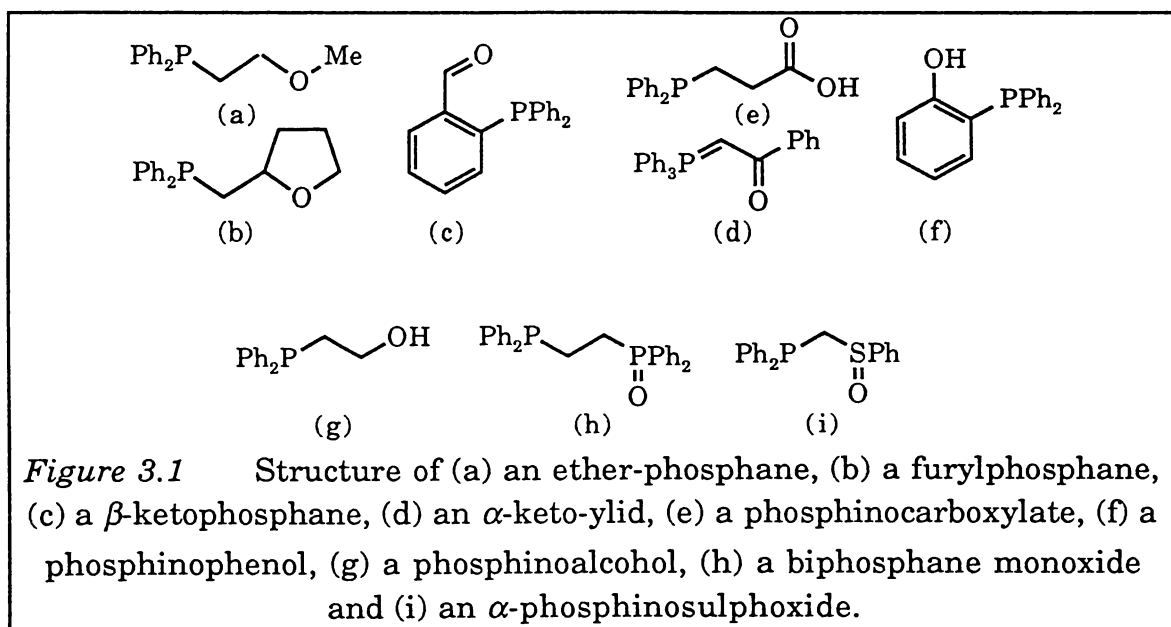
A bidentate ligand containing both phosphorus and oxygen donor atoms would provide both the labile solvent function and the tertiary phosphane selectivity effect in one molecule.

This type of ligand is playing an important role in the development of homogeneous catalysts. Examples include the selective nickel-catalysed polymerisation of ethene;^[4] the hydrocarbonylation of methanol

to acetic acid,^[5,6] acetaldehyde,^[6,7] or ethanol;^[8] and the stereoselective hydrogenations,^[9] hydrosilations,^[10] and hydroformylations.^[11]

Most of these bidentate O,P ligands consist of tertiary phosphorus atoms with ketone, alcohol or carboxylate oxygen atoms, or with ether oxygen atoms in either open-chain or cyclic moieties. These oxygen donors, in the solvent role discussed above form only weak metal-oxygen bonds, which may be broken and reformed without loss of the oxygen donor from the complex.^[14] Thus these hemilabile^[12] or hybrid ligands^[13] form vacant coordination sites as necessary during the catalytic cycles.

These O,P ligands can be broadly divided into five classes: (i) ether-phosphanes and furylphosphanes; (ii) β -ketophosphanes and α -keto-ylids; (iii) phosphinocarboxylates; (iv) phosphinoalcohols and phosphinophenols; and (v) biphosphane monoxides and α -phosphinosulphoxides. Illustrative examples of these ligands are shown in Figure 3.1.



Ether-phosphanes are one of the most extensively studied class of oxygen-containing functionalised phosphanes. A survey of widely used ether-phosphanes has been recently published.^[3] In many cases the

oxygen donors are part of simple acyclic^[12,15] or cyclic^[8,15] ether moieties such as shown in Figure 3.1. Related to these are various, potentially multidentate phosphanes with polyether chains,^[16,17] which have also been shown to exhibit phase-transfer properties.^[17] Macrocycles containing O,P donor atoms have also been studied. These include crown-ethers which contain exocyclic phosphane substituents^[18] and macrocycles consisting of oxygen and phosphorus atoms which are both part of the framework.^[19] This forces O and P contact with the transition metals within the cavity in unusual geometries.

In comparison, the β -ketophosphanes have been less extensively investigated. These phosphanes have been shown to form both unidentate complexes and stable five-membered chelate rings by complexation of a metal species. The chelated phosphane compounds are capable of enolisation. Deprotonation by base^[20] or reaction with Ni(0) complexes^[21] leads to the corresponding bidentate phosphinoenolates. In contrast to the tervalent phosphorus compounds, the pentavalent α -keto-ylids^[22] are not able to coordinate via the phosphorus atom. Coordination is conceivable via the ylidic carbon atom.^[23] However, the reaction of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{Ph}$ with Ni(0) complexes has produced phosphorus-coordinated species via P-Ph bond cleavage.^[24]

Neutral phosphinocarboxylates, as found for their β -keto-phosphane analogues, coordinate in either chelating conformations or unidentately through the phosphorus atom. Also used are the carbanions of carboxylic esters and salts of the free acids. These coordinate either in a chelating or bridging mode.^[25] The complexation properties of the free phosphinocarboxylic acids is pH- and solvent-polarity-dependent; hence the investigation of the coordination chemistry of O,P ligands in aqueous solution is feasible.^[26]

Phosphinoalcohols and phosphinophenols are usually deprotonated to the respective alkoxides and phenoxides.^[27] Biphosphane monoxides are derivatives of biphosphanes in which one tervalent phosphorus remains and the other becomes pentavalent and doubly bonded to an oxygen atom. This oxygen atom is available for coordination along with the remaining tervalent phosphorus atom. The α -phosphinosulphoxides are closely related to the biphosphane monoxides with the pentavalent phosphorus atom being replaced by a sulphur atom.^[28] However, these are prone to isomerisation with the oxygen atom being transferred from the sulphur to the phosphorus atom.^[29]

β -ketophosphanes like (2-diphenylphosphino)benzaldehyde (PC(O)H) exhibit a variety of reactivities on metal centres. The thermolysis of $\text{cis-PtCl}_2(\text{PC(O)H})_2$, which contains only monodentate P-bound phosphanes, affords the bright yellow complex $\text{PtCl}(\eta^2\text{-PCO})(\text{PC(O)H})$ ^[30] with the evolution of HCl. $\text{PtCl}(\eta^2\text{-PCO})(\text{PC(O)H})$ contains one monodentate P-bound phosphane and one bidentate P- and C-bound phosphane where the Pt atom replaces the H atom from the aldehyde functionality. The addition of PC(O)H to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ affords the iridium complex $\text{IrCl}(\eta^2\text{-PCO})\text{CO}(\text{H})(\text{PPh}_3)$ ^[30] in which the bidentate phosphane is bound in a similar manner. Thermolysis of this complex leads to decarbonylation and formation of the starting complex wherein one triphenylphosphane ligand is derived from the aldehyde. In contrast to these results, the reaction of the same phosphane with ruthenium trichloride hydrate affords the bisaldehyde complex $\text{RuCl}_2(\eta^2\text{-PC(O)H})_2$ ^[30] in which the bidentate aldehyde ligands remains intact and bonded to the ruthenium atom via the P and O atoms. Thermolysis of this complex leads to $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ in which the CO groups have been eliminated from the phosphane ligand, but remain bonded to the ruthenium atom.^[30] The formation of these complexes is thought to proceed with the formation of a

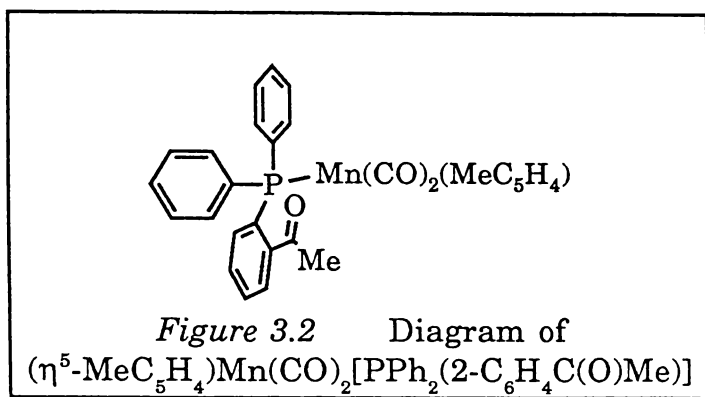
π -bonded carbonyl which can then rearrange via hydrogen migration to give the product.

This proposed π -bonded formyl group is similar to the well-known phosphinostyrene chelates derived from the 2-styryldiphenylphosphane ($\text{Ph}_2\text{P}(\text{2-C}_6\text{H}_4\text{CH}=\text{CH}_2), (\text{sp})$) ligand.^[31-34] While thermolysis reactions of sp with $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$) generally lead to mono-nuclear complexes such as $\text{M}(\text{CO})_3(\text{sp})$,^[32] in which the sp ligand is bidentate, reactions under less forcing conditions (radical-ion initiated reactions) generally maintain the triangular metallic core.^[33,34] The radical-ion initiated reaction between sp and $\text{Ru}_3(\text{CO})_{12}$ affords the cluster $\text{Ru}_3(\text{CO})_{10}(\text{sp})$, which contains the olefinic tertiary phosphane bridging two metal atoms. The phosphorus atom is bonded to one Ru atom and the olefin is π -bonded to the other. Gentle heating converts this complex to $\text{H}_2\text{Ru}_3(\mu_3\text{-HCCC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$, which contains an acetylenic tertiary phosphine bridging all three metal atoms as a result of oxidative addition of two C-H bonds to the Ru_3 core. Further dehydrogenation of $\text{H}_2\text{Ru}_3(\mu_3\text{-HCCC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$ in a reaction with $\text{Ru}_3(\text{CO})_{12}$ affords the tetra-nuclear cluster $\text{Ru}_4(\mu_4\text{-HC}_2\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})_{11}$ ^[34] in which the four ruthenium and two alkene carbon atoms form a distorted octahedron with the phosphorus atom of the former sp ligand still bonded to one of the ruthenium atoms.

Reactions of the ketophosphane $\text{Ph}_2\text{PCH}_2\text{C(O)Ph}$ (PCCO) with $\text{Ru}_3(\text{CO})_{12}$ afford the monodentate phosphane derivatives $\text{Ru}_3(\text{CO})_{12-n}(\text{PCCO})_n$ ($n = 1, 2$).^[35] In the presence of $[\text{PPN}][\text{OAc}]$ the phosphane ligand bends over displacing a second carbonyl to give $\text{Ru}_3(\text{CO})_{10}(\mu\text{-PCCO})$, in which the functional phosphane acts as a P,O bridging ligand.

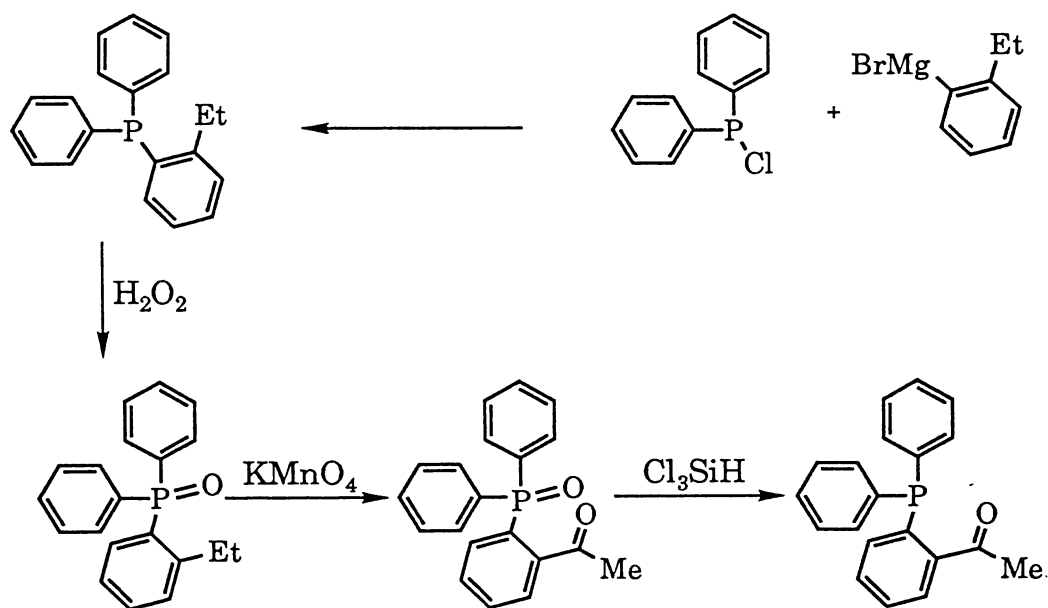
In this chapter the synthesis and some reactions of methyl-substituted β -ketophosphanes will be presented.

3.2 PREPARATION OF THE PHOSPHANE LIGANDS



Ortho-acetylated phenylphosphanes have been prepared by two groups previously. The first method involved assembling the ligand on the metal atom, but the yields were

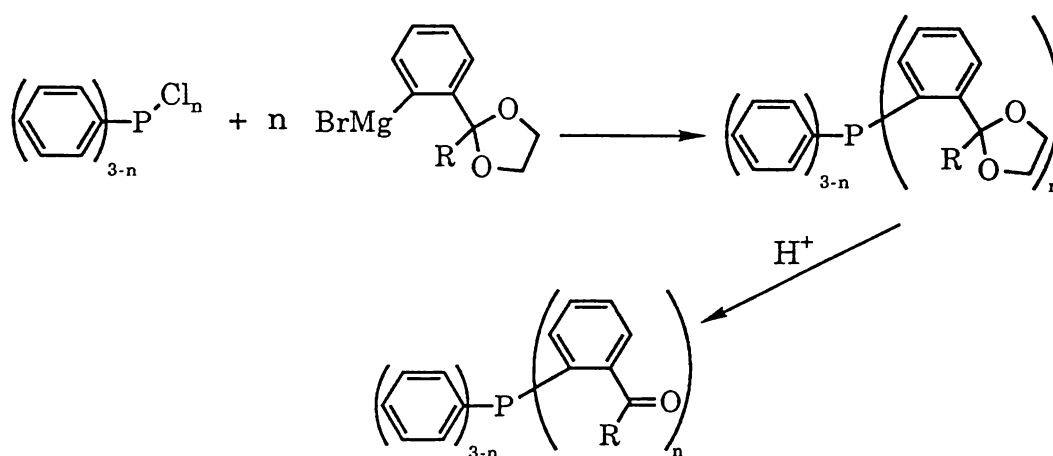
low and the phosphane remained attached to the template metal atom, as shown in Figure 3.2.^[36] The second group used two different multi-step syntheses. The first of these methods (see Scheme 3.1), started with coupling a chlorophenylphosphane and an *o*-ethylbenzene with subsequent oxidation of both the phosphorus and the ethyl groups followed by reduction at the phosphorus atom.^[37] Except for the oxidation of the *o*-ethylphosphane to the *o*-acetylphosphane this method was closely adhered to in the following preparations.



Scheme 3.1

The second method involved reaction of the Grignard of dioxolanes (ethylene ketals of bromobenzaldehydes or bromoacetophenones) with

[PPh_{3-n}Cl_n] and treating the resulting phosphanes with 4-MeC₆H₄SO₃H in acetone^[38] as shown in Scheme 3.2. The difficulty with this method is in the protection of the arylketone. Of the many methods attempted in this current work to effect this protection, refluxing of 2'-BrC₆H₄COMe, (CH₂OH)₂ and 4-MeC₆H₄SO₃H in toluene in a Dean-Stark trap gave the best results. However, the highest purity bromoacetophenone ethylene ketal obtained using this method was 89 %, which was not pure enough to continue with the Grignard reaction given that the major impurity was the unprotected ketone.



Scheme 3.2

3.2.1 Experimental

All of the phosphane reactions discussed below were carried out on a Schlenk line in an atmosphere of nitrogen, with the exception of oxidation of phosphorus(III) to phosphorus(V) with hydrogen peroxide. When samples were required for nmr analysis, analytical grade solvents were used and single straight-chain hydrocarbons were substituted for the petroleum spirit solvents. Otherwise dried laboratory-grade solvents were used for both reaction media and extractions.

3.2.2 Preparation of 2-ethylphenyldiphenylphosphane

2-bromoethylbenzene (18.5 g, 0.1 mol) was added dropwise to Mg turnings (2.3 g, 0.1 mol) in THF (150 ml) held at 30-40°C. In order to ensure completion of the Grignard reaction the solution was stirred for

30 minutes at 50°C and then cooled to between -10 and 0°C. PPh_2Cl (22.0 g, 0.1 mol) in THF (80 ml) was added dropwise to the solution. The solution was stirred at room temperature for 30 minutes and heated to 50°C for 5 minutes. The mixture was cooled to between -10 and 0°C, H_2SO_4 (55 ml, 2 mol l^{-1}) was added and the mixture stirred at room temperature for 20 minutes. The resulting mixture was extracted with benzene (4 x 50 ml), and the combined extracts were washed with saturated aqueous NaHCO_3 (50 ml), water (2 x 50 ml) and dried with magnesium sulphate. Recrystallisation from methanol yielded 2-ethylphenyldiphenylphosphane (20.0 g, 69 %); GC mass spectrum m/e 290 (M)⁺ and m/e 289 ($M - \text{H}$)⁺

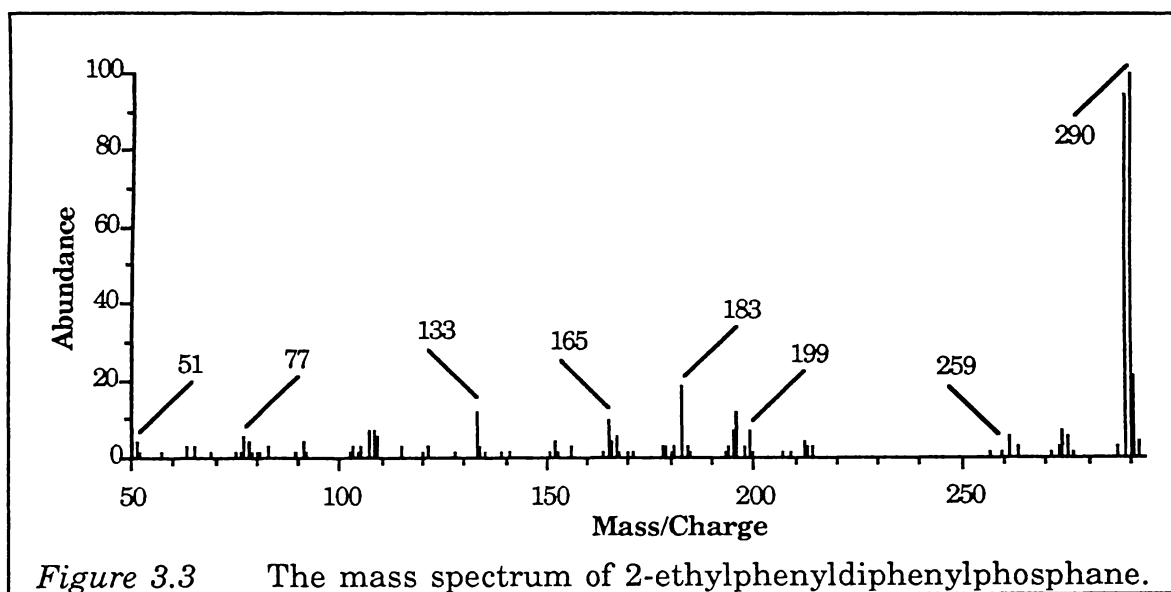
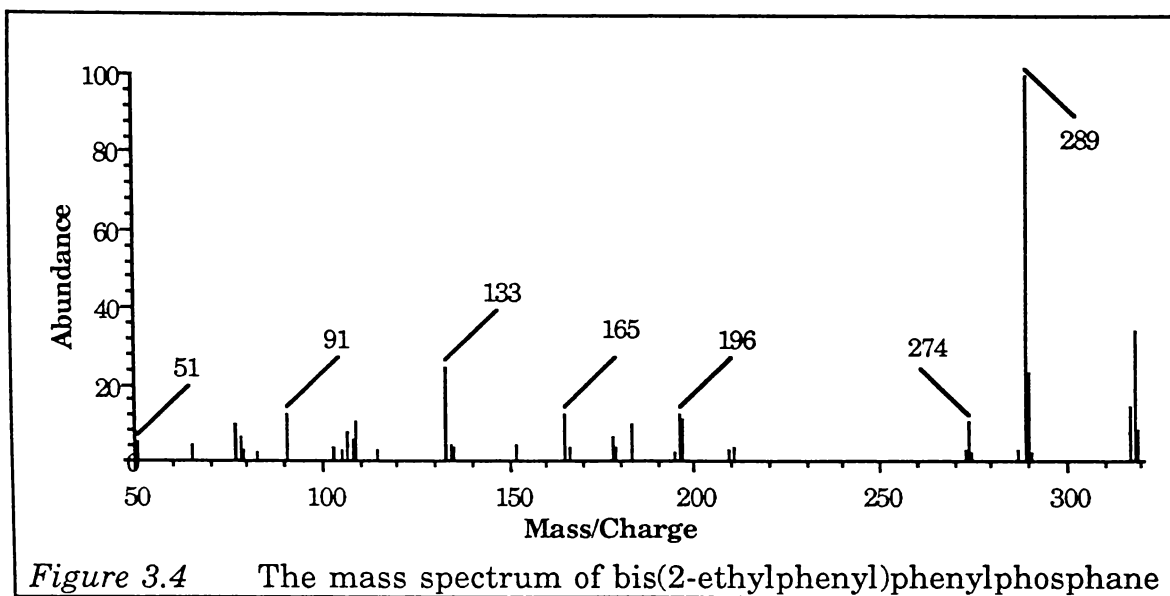


Figure 3.3 The mass spectrum of 2-ethylphenyldiphenylphosphane.

3.2.3 Preparation of bis(2-ethylphenyl)phenylphosphane

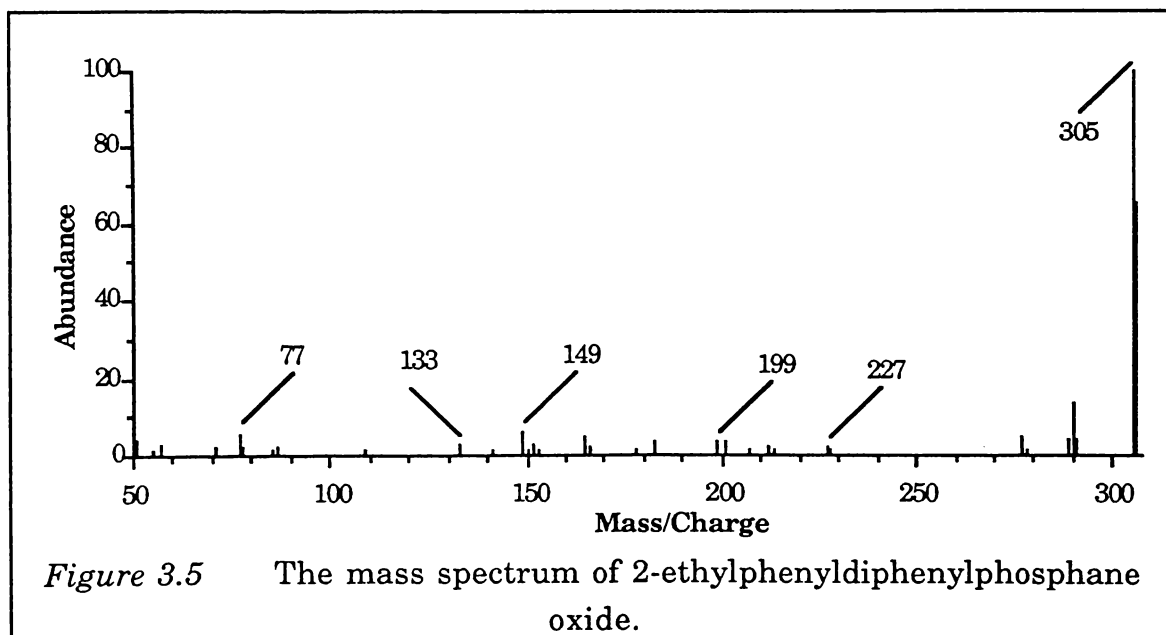
For the preparation of bis(2-ethylphenyl)phenylphosphane the same method was used, with quantities and reaction times as for the synthesis of 2-ethylphenyldiphenylphosphane with the following changes. 2-bromoethylbenzene (9.25 g, 50.0 mmol), Mg (1.21 g, 50.0 mmol) in THF (75 ml), PPhCl_2 (4.48 g, 25.0 mmol) in THF (20 ml), H_2SO_4 (25 ml) extracted with benzene (3 x 50 ml). After washing the solvent was removed and the product used directly for the hydrogen peroxide oxidation.

GC mass spectrum (see Figure 3.4) m/e 318 (M)⁺; m/e 289 ($M - Et$)⁺ and m/e 274 ($M - Et - Me$)⁺



3.2.4 Preparation of 2-ethylphenyldiphenylphosphane oxide

A slight excess of H_2O_2 (3 ml of 27 %) was added dropwise to 2-ethylphenyldiphenylphosphane (6.6 g, 22.8 mmol) in acetone (75 ml) over a period of 10 minutes. The volume was reduced under vacuum and the remaining solution added to chloroform (100 ml), washed with water (4 x 50 ml) and dried with $MgSO_4$. Recrystallisation from a minimum of chloroform yielded 2-ethylphenyldiphenylphosphane oxide (6.89 g, 99 %)



characterised by GC mass spectrum m/e 305 ($M - H$)⁺ (see Figure 3.5).

3.2.5 Preparation of bis(2-ethylphenyl)phenylphosphane oxide

The crude bis(2-ethylphenyl)phenylphosphane was dissolved in acetone (80 ml) and oxidised with a slight excess of H_2O_2 (6 ml of 27 %). The volume was reduced and the residue added to chloroform (100 ml), washed with water (4 x 50 ml), dried with $MgSO_4$ and recrystallised from chloroform. Yield of bis(2-ethylphenyl)phenylphosphane oxide was 5.63 g, 67 %, for both steps.

GC mass spectrum (see Figure 3.6) m/e 334 (M)⁺; m/e 305 ($M - Et$)⁺ and m/e 290 ($M - Et - Me$)⁺

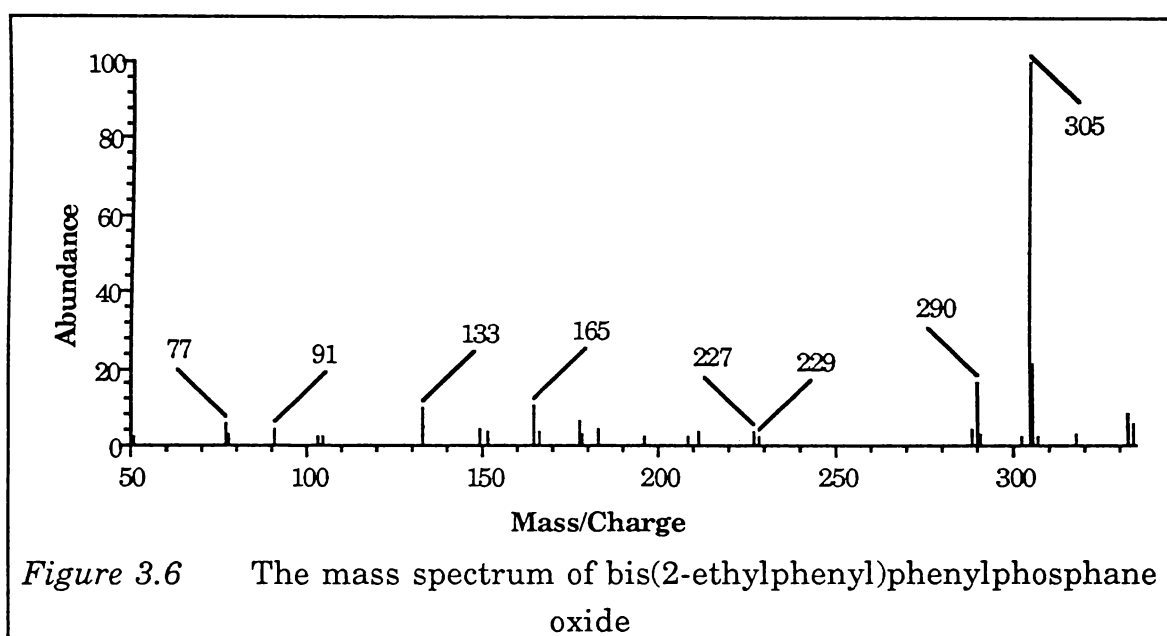


Figure 3.6 The mass spectrum of bis(2-ethylphenyl)phenylphosphane oxide

3.2.6 Preparation of 2-acetylphenyldiphenylphosphane oxide

A small excess of CrO_3 (0.5 g) dissolved in a minimum volume of glacial acetic acid was added in 4 aliquots over 24 hours to a solution of 2-ethylphenyldiphenylphosphane oxide (1.0 g, 3.26 mmol) in glacial acetic acid (50 ml) stirred at 30°C. The progress of the reaction was monitored by analysis by GC-MS of small aliquots of the reaction mixture. In general conversion of the 2-ethylphenyldiphenylphosphane oxide was complete within 24 hours.

The reaction mixture was poured into water (50 ml) and extracted with ethyl acetate (4 x 25 ml). The solvent was removed under reduced pressure from the combined extracts. The resulting green residue was dissolved in a minimum of methanol (~30 ml) which, upon addition of water (60 ml), gave a pale green solution with a fine white colloid. The combined chloroform extracts (5 x 30 ml) were dried with MgSO_4 and filtered to give spectroscopically pure 2-acetylphenyldiphenylphosphane oxide (0.65 g, 62 %). This compound was characterised by its GC mass spectrum m/e 320 (M)⁺, m/e 305 ($M - \text{Me}$)⁺ and m/e 277 ($M - \text{COMe}$)⁺ (see Figure 3.7).

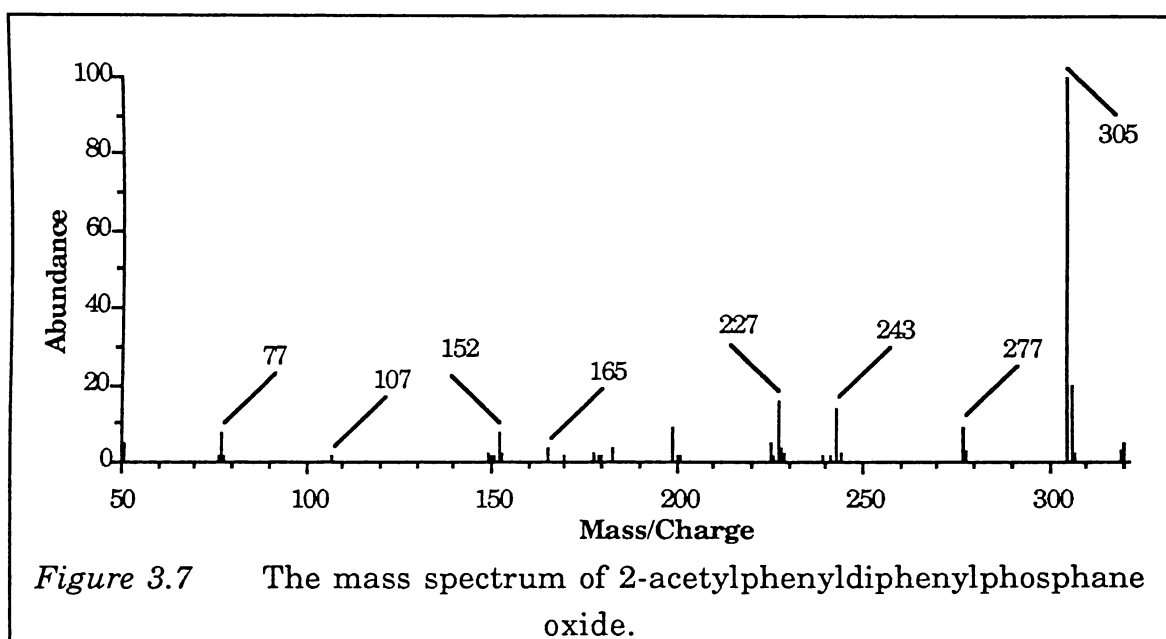
Further runs were carried out at differing temperatures in attempts to improve the yield of 2-acetylphenyldiphenylphosphane oxide. Reaction conditions for these runs are shown in Table 3.1 and product yields in Table 3.2. In the room temperature reactions, as represented by run 2, the oxidation was irregular. If oxidation products were observed

Table 3.1 Reaction quantities and conditions for the oxidation of 2-ethylphenyldiphenylphosphane oxide with CrO ₃ in acetic acid.					
Run	Phosphane (mmol)	CrO ₃ (mmol)	Volume of solvent used (ml)	Temperature (°C)	Reaction time (hours)
1	3.26	38.0	30	40	6
2	1.63	excess	25	20-25	48
3	3.26	excess	50	30	24

Table 3.2 Yields obtained from the oxidation of 2-ethylphenyldiphenylphosphane oxide with CrO ₃ .				
Run	Ph ₂ P(O)– C ₆ H ₄ COOH (mmol, %)	Ph ₂ P(O)– C ₆ H ₄ COMe (mmol, %)	Ph ₂ P(O)C ₆ H ₄ Et (mmol, %)	Ph ₂ P(O)OH (mmol, %)
1	2.50, 76.7	0.40, 12.3	0.05, 1.5	0.36, 11.0
2	0.12, 7.5	0.82, 50.3	0.02, 1.2	-
3	(1)	2.02, 62.0	(1)	(1)
(1). Not measured.				

then yields are given in Table 3.2, but in some cases no oxidation was observed.

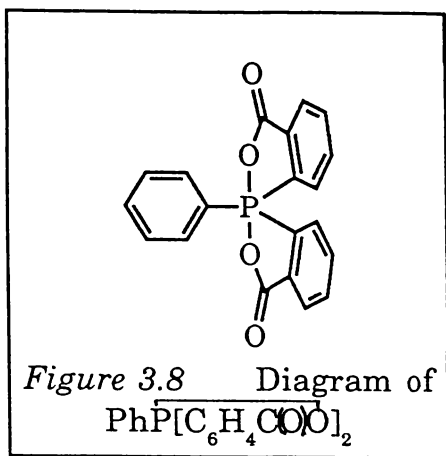
As would be expected the yield of oxidation products increases as the reaction temperatures increase from room temperature (58 %) through 30°C (62 %) to 40°C (89 %). Yields of 2-acetylphenyldiphenylphosphane oxide were maximised at a reaction temperature of 30°C. At the higher temperature oxidation did not stop at the ketone, and further oxidation occurred with conversion of the methyl ketone to a carboxylic acid group.



3.2.7 Oxidation of bis(2-ethylphenyl)phenylphosphane oxide

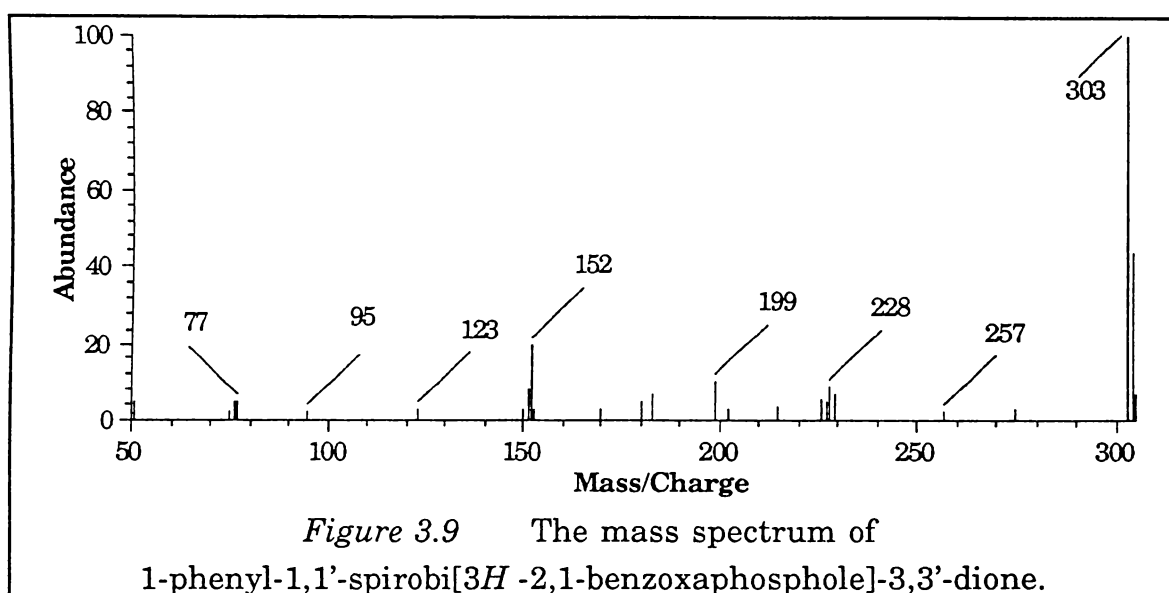
A small excess of CrO_3 (0.9 g) dissolved in a minimum of glacial acetic acid was added in 4 aliquots over 84 hours to a stirred solution of bis(2-ethylphenyl)phenylphosphane oxide (1.0 g, 2.99 mmol) in glacial acetic acid (50 ml) at 30°C.

The reaction mixture was poured into water (100 ml) and extracted with dichloromethane (4 x 25 ml). The solvent was removed under reduced pressure from the combined extracts. The resulting residue was washed with diethyl ether (4 x 20 ml) to leave 0.74 grams of a



white solid. The white solid was characterised as 1-phenyl-1,1'-spirobi[3H-2,1-benzoxaphosphole]-3,3'-dione (67 %) (see Figure 3.8) by a full X-ray crystal structure determination (see Section 3.3) and by its GC mass spectrum m/e 304 ($M - \text{CO}_2$)⁺ and m/e 303 ($M - \text{CO}_2\text{H}$)⁺ (see Section 3.2.7.1).

3.2.7.1 GC-MS of 1-phenyl-1,1'-spirobi[3H-2,1-benzoxaphosphole]-3,3'-dione



The mass spectrum of $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$, as shown in Figure 3.9, is reasonably simple. Only two peaks greater than 30 % are evident. These are the highest observed fragment at m/e 304 which corresponds to loss of CO_2 from the molecular ion and the base peak at m/e 303 ($M - \text{CO}_2\text{H}$)⁺

3.2.8 Preparation of 2-acetylphenyldiphenylphosphane

2-acetylphenyldiphenylphosphane oxide (0.28 g, 0.87 mmol) and SiHCl_3 (0.26 ml, 0.35 g, 2.6 mmol) in sodium-dried benzene (50 ml) were refluxed for 4 hours and cooled in ice. The ice cold solution was neutralised with a slight excess of NaOH (30 % aqueous). The resulting

mixture was extracted with benzene (6 x 30 ml) and the combined extracts dried with MgSO_4 . The benzene was removed under reduced pressure to yield, as a yellow solid, 2-acetylphenyldiphenylphosphane (0.25 g, 94 %). ^{13}C nmr (δ 200.7 s, 143.8 s, 134.3 d, 132.6 s, 131.6 d, 131.3 d, 131.3 d, 131.2 d, 130.3 s, 129.8 d, 127.8 d and 28.9 q) (see Section 3.2.8.1), ^1H nmr (δ 7.63 m, 7.47 m and 2.44 s) (see Section 3.2.8.2), ^{31}P nmr (δ -5.17 s), GC mass spectrum m/e 304 (M)⁺; 227 (M - Ph)⁺; 183 (M - Ph - MeCOH)⁺; 149 (M - Ph - C_6H_6)⁺; 107 (M - Ph - PhCOMe)⁺ and 77 (M - PhPC $_6\text{H}_4$ COMe)⁺ (see Figure 3.10).

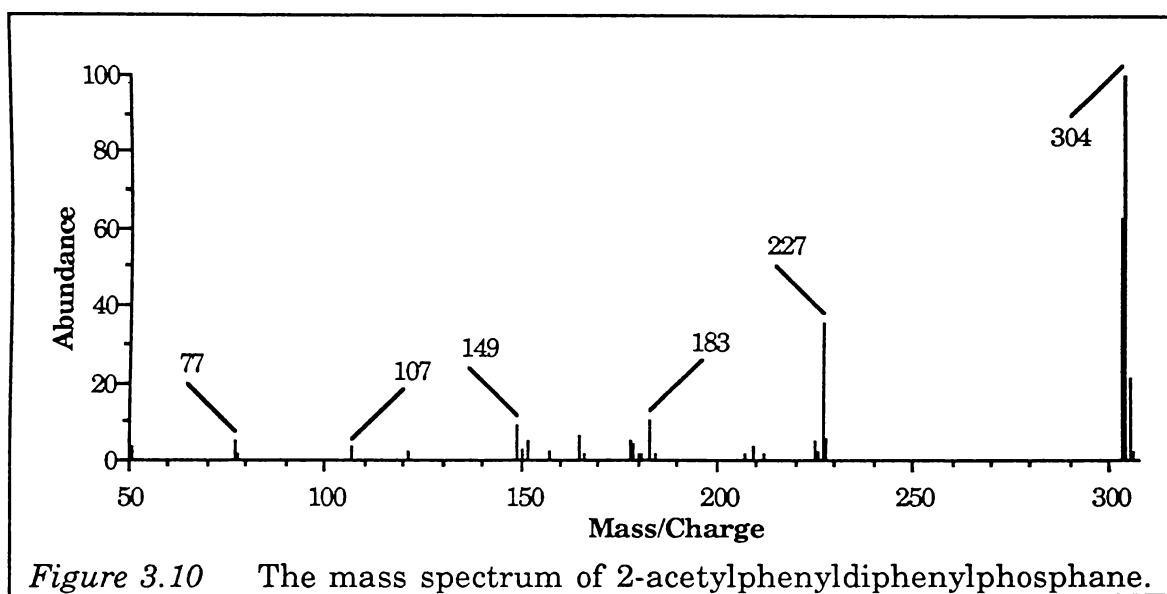


Figure 3.10 The mass spectrum of 2-acetylphenyldiphenylphosphane.

3.2.8.1 ^{13}C nmr of 2-acetylphenyldiphenylphosphane

The proton decoupled ^{13}C nmr spectrum of 2-acetylphenyldiphenylphosphane was recorded in CDCl_3 . The coupling and assignments are given in Table 3.3 and the spectrum is shown Appendix 4.

3.2.8.2 ^1H nmr of 2-acetylphenyldiphenylphosphane

The ^1H nmr spectrum of 2-acetylphenyldiphenylphosphane, as recorded in CDCl_3 solvent, is consistent with the above formulation. Signals are observed in only two areas of the spectrum: the first is a group of multiplets at δ 7.63 and 7.47 ppm arising from the fourteen aryl protons

Table 3.3 ^{13}C nmr spectrum for $\text{Ph}_2\text{P}[\text{C}_6\text{H}_4\text{COMe}]$				
δ (ppm)	Multiplicities		$J(^{31}\text{P})$ (Hz)	Assignment
	^1H	^{31}P		
200.7	s	s	-	11
143.8	s	d	6.4	4
134.3	d	d	10.4	5,7 or 8
132.6	s	d	103.9	10
131.6	d	s	-	6
~131.3	d	d	~9	5,7 or 8 [‡]
131.3	d	d	9.8	1 or 2
131.2	d	s	-	3
130.3	s	d	99.7	9
129.8	d	d	11.8	5,7 or 8
127.8	d	d	8.0	1 or 2
28.9	q	s	-	12

‡ Not observed, signal masked by strong signals from carbons 1 or 2 and 3.

and a narrow singlet at δ 2.44 ppm associated with the three methyl protons. The spectrum is shown in Appendix 4.

3.2.8.4 Vibrational spectroscopy of 2-acetylphenyldiphenylphosphane

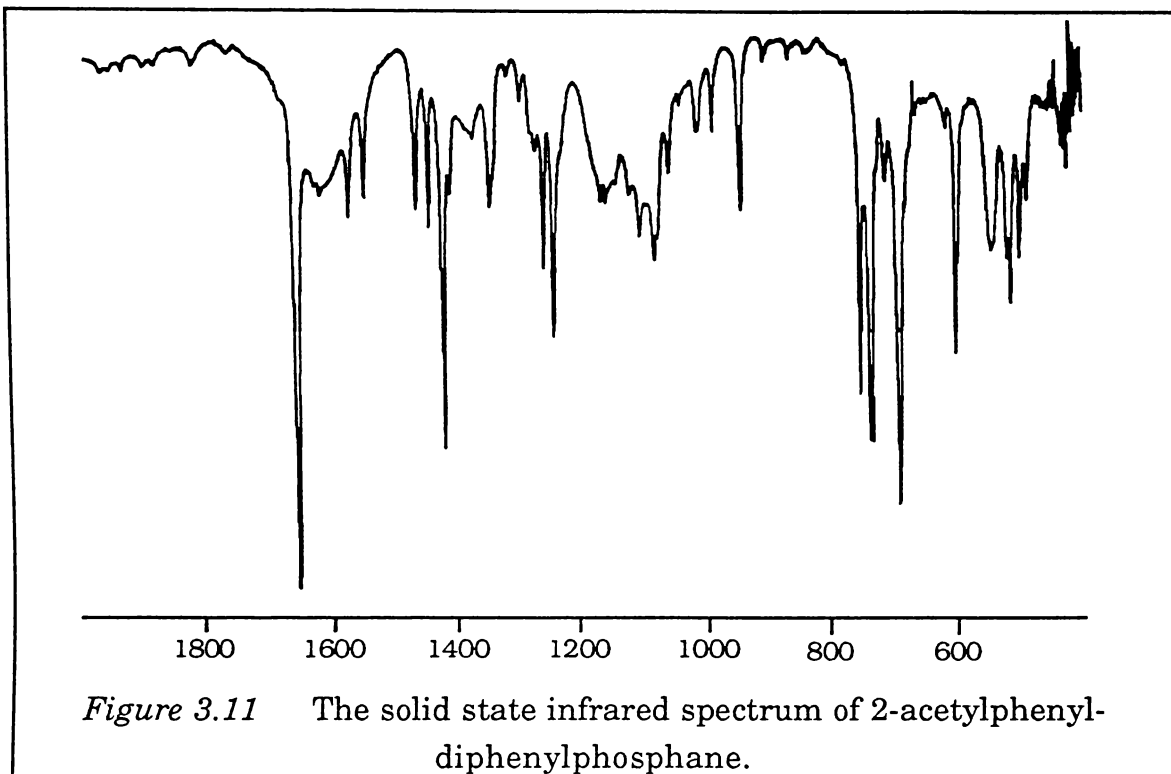
The solid infrared spectrum of 2-acetylphenyldiphenylphosphane was recorded as a KBr disc in the 2000 to 400 cm^{-1} region (see Figure 3.11). The most intense peak in this region (1670 cm^{-1}) can be assigned to the stretching vibration of the carbonyl group. Peaks at 764, 745 and 701 cm^{-1} are consistent with mono- and 1,2-di-substitution of a phenyl ring.

3.3 $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$, AN X-RAY CRYSTALLOGRAPHIC STUDY

3.3.1 Data Collection

Colourless, wedge shaped crystals were grown from a solution in toluene, which had been cooled to -10°C from room temperature.

One of the few well-formed crystals was attached to a fine glass fibre with grease and mounted on a goniometer. Preliminary precession photography indicated a space group of $P1$ or $P\bar{1}$.



The same crystal, of dimensions 0.50 x 0.20 x 0.05 mm, was sent to the University of Canterbury for intensity data collection. Using a Nicolet P3 diffractometer with zirconium filtered Mo-K_{α} radiation, a total of 3274 unique reflections were collected within the range of $5^{\circ} < 2\theta < 21^{\circ}$. Data were collected in $P\bar{1}$ with $a = 8.505(6)$, $b = 13.359(10)$ and $c = 15.187(8)$ Å, $\alpha = 83.07(5)$, $\beta = 90.02(5)$ and $\gamma = 71.38(5)^{\circ}$, $U = 1622(2)\text{Å}^3$ and $Z = 4$. Further analysis indicated monoclinic symmetry with systematic absences consistent with space group $C2/c$, to which the data were transformed. The resulting crystal data are given in Table 3.4. All reflections with $I < 0.5\sigma$ were replaced by 0.25σ . This left 929 reflections with $I > 2.0\sigma(I)$ which were used in all the calculations.

Table 3.4 Crystal data for $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$.

Molecular formula : $\text{C}_{20}\text{H}_{13}\text{O}_4\text{P}$

M = 348.297

Crystal class : Monoclinic

Space group : *C* 2/c

a = 25.320(5) *U* = 3243(4)

b = 8.505(2) *Z* = 8

c = 15.187(3) *F*(000) = 1440

β = 97.32(3) *D*_{calc} = 1.426 g cm⁻³

X-rays : Mo-K α (λ = 0.710 73 Å)

Temperature of collection : -100°C

Linear absorption coefficient (μ) : 1.46 cm⁻¹

3.3.2 Solution and Refinement

The structure was solved using the TREF direct method routine of SHELXS86.^[39] This revealed all non-hydrogen atoms. The phosphorus atom was assigned an anisotropic temperature factor in the final cycles, whereas the carbon and oxygen atoms were left isotropic. The hydrogen atoms were fixed at 98 pm from the attached carbon atom.

After introduction of a weighting scheme the refinement converged to give *R* = 0.0957 with *R*_w = 0.0825 and $w = (\sigma^2(F) + 0.000\,562F^2)^{-1}$. The thermal parameters of the atom centres were all of reasonable values with *U*_{iso} (C) ranging from 0.0101 to 0.0379 and for oxygen from 0.0210 to 0.0316.

The final difference map showed some residual electron density of ca. 0.65 e Å⁻³ near the phosphorus atom. This can be attributed to

difficulties with absorption corrections and a weakly diffracting crystal. This is also reflected by the higher than usual R factors. No parameter shifted by more than two percent of its estimated standard deviation in the final refinement cycle.

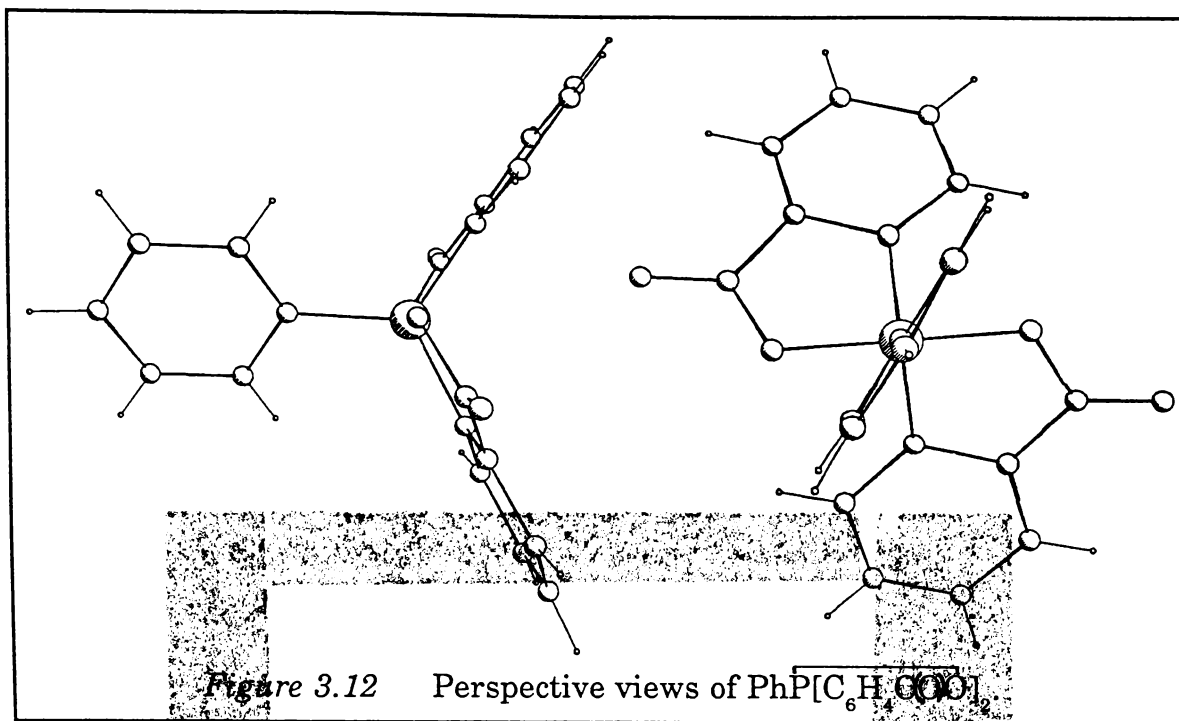
Selected bond lengths and angles are given in Table 3.5, all bond lengths and angles, the final positional parameters and final thermal parameters in Appendix 3.

3.3.3 Discussion of the Structure of $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$

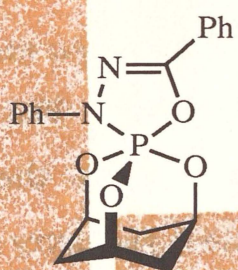
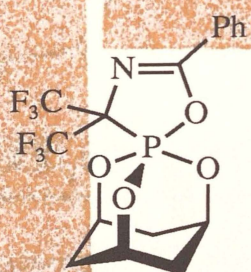
The structure of $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$, which had been previously determined by Rivera and Sheldrick,^[40] consists of discrete molecules. Perspective views of $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$ are shown in Figure 3.12.

Table 3.5 Selected bond lengths and angles for $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$.

Bond Lengths (pm)			
P(1)---C(11)	181.3(12)	C(22)---C(27)	148.3(16)
P(1)---C(21)	181.3(12)	O(21)---C(27)	123.0(13)
P(1)---O(22)	179.2(9)	O(22)---C(27)	132.9(15)
P(1)---C(31)	181.0(11)	C(32)---C(37)	144.4(16)
P(1)---O(32)	178.3(8)	O(31)---C(37)	122.7(13)
C(Ph)---C(Ph)	135.3(17)-142.5(17)	O(32)---C(37)	138.0(14)
Bond Angles (°)			
C(21)-P(1)-C(11)	120.1(5)	C(27)-C(22)-C(21)	111.1(10)
O(22)-P(1)-C(11)	90.1(5)	C(27)-C(22)-C(23)	127.3(11)
O(22)-P(1)-C(21)	88.2(5)	O(21)-C(27)-C(22)	125.1(12)
C(31)-P(1)-C(11)	118.7(5)	O(22)-C(27)-C(22)	112.6(11)
C(31)-P(1)-C(21)	121.2(5)	O(22)-C(27)-O(21)	122.2(11)
C(31)-P(1)-O(22)	91.3(4)	C(27)-O(22)-P(1)	115.8(8)
O(32)-P(1)-C(11)	90.3(5)	C(37)-C(32)-C(31)	115.1(15)
O(32)-P(1)-C(21)	91.0(5)	C(37)-C(32)-C(33)	124.1(11)
O(32)-P(1)-O(22)	179.2(5)	O(31)-C(37)-C(32)	128.3(12)
O(32)-P(1)-C(31)	89.1(4)	O(32)-C(37)-C(32)	110.6(10)
C(Ph)-C(Ph)-C(Ph)	117.1(12)	O(32)-C(37)-O(31)	120.9(11)
	-122.9(11)	C(37)-O(32)-P(1)	114.3(7)



The overall geometry of $\text{PhP}[\text{C}_6\text{H}_4(\text{COO})]_2$ consists of a central phosphorus atom bonded to three carbon and two oxygen atoms in what is close to an ideal trigonal bipyramidal arrangement. The oxygen atoms occupy the two axial sites, as is normally the case for the more electronegative substituents. Near trigonal bipyramidal geometry is indicated by the O-P-C bond angles (range 88.2 to 91.8°), the C-P-C bond angles (range 118.7 to 121.2°) and the O-P-O bond angle (179.2(5)°) being close to the ideal values of 90, 120 and 180° respectively. One of the attached carbon atoms is contributed by a phenyl group with the remaining carbon and oxygen atoms being contributed by two bidentate $\text{C}_6\text{H}_4(\text{COO})$ moieties. Each of the three groups attached to P is approximately planar with the maximum atom-least square plane distance for each plane being 22, 44 and 45 pm respectively. The two larger deviations are reduced to only 1 and 3 pm when the COO functionalities are excluded from the calculations. Looking along the C(11)-P(1) bond (around which there is an approximate twofold symmetry axis) shows the phenyl ring to be staggered with respect to the two benzoate residues, forcing the phenyl ring to twist out of the equatorial plane by 37°. This arrangement is more



than likely due to intermolecular interactions between neighbouring molecules in the lattice as there are no short non-bonding intramolecular interactions evident. The C-C bond lengths (range 135.3(17) to 142.5(17) pm) and C-C-C bond angles (range 117.1(12) to 122.9(11) °) within the phenyl rings are consistent with sp^2 -hybridised carbon atoms. The C(22)-C(27) and C(32)-C(37) bond lengths of 148.3(16) and 144.4(16) pm respectively are consistent with single bonds between sp^2 -hybridised carbon atoms. This indicates little or no electron delocalisation within the two five-membered $\overline{\text{C-O-P-C-C}}$ rings. The P(1)-C(21) and P(1)-C(31) bond lengths (181.3(12) and 181.0(11) pm) are the same as the phenyl C-P bond length of 181.3(12) pm which supports this lack of delocalisation, as do the C-O bond lengths within the ring. These distances of 132.9(15) and 138.0(14) pm are as would be expected in carboxylic acid type systems. The carbonyl C-O bond lengths of 123.0(13) and 122.7(13) pm are also standard for these systems.

The bond lengths and angles found in a previous, more precise determination are comparable to those found in this study.^[40] All but one of the bond lengths are within 2σ of their analogue in the other determination.

The unstrained geometry found for $\text{Ph}\overline{\text{P}[\text{C}_6\text{H}_4\text{COO}]_2}$ is not reflected by other phosphoranes studied by X-ray crystallography: a much greater deviation from trigonal bipyramidal coordination is found for $\overline{\text{P}[\text{N}(\text{C}_6\text{H}_3\text{Me}_2)\text{C}_6\text{H}_4\text{O}](\text{OMe})_3}$ ^[41] and the caged polycyclic tetraoxyphosphoranes $(\text{PO}_4\text{C})(\text{C}_6\text{H}_5\text{CN})(\text{CF}_3)_2(\text{C}_6\text{H}_9)$ ^[42] and $(\text{PO}_4\text{N})(\text{C}_6\text{H}_5\text{CN})(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_9)$ ^[43] with square pyramidal coordination for the bicyclic $[\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}]\overline{\text{P}[\text{CMe}_2\text{CH}_2\text{CMe}_2]\text{C}_6\text{H}_4\text{Br}}$ ^[44] Similar ligand arrangements are found in $\overline{\text{S}[\text{C}_6\text{H}_4\text{COO}]_2}$ ^[45] and $\overline{\text{Se}[\text{C}_6\text{H}_4\text{COO}]_2}$ ^[46] However replacement of the phenyl group by a lone pair causes much larger deviations from idealised trigonal bipyramidal geometry.

3.4 DISCUSSION

There are a number of possible routes for the synthesis of $\text{Ph}_2\text{P}[\text{C}_6\text{H}_4\text{COMe}]$. Four methods were attempted before a successful method was discovered. The first method involved the $(\text{MeCN})_2\text{PdCl}_2$ catalysed reaction of 2'-bromoacetophenone with $\text{Ph}_2\text{PSiMe}_3$. The $\text{Ph}_2\text{PSiMe}_3$ was prepared in good yields from PPh_3 , lithium and Me_3SiCl .^[47] However the reaction of 2'-bromoacetophenone with $\text{Ph}_2\text{PSiMe}_3$ did not proceed smoothly to the desired product. Instead at lower temperatures, up to 105 °C, the starting materials were isolated and at higher temperatures the major product isolated was Ph_3PO .

The second method involved conversion of 2'-bromoacetophenone ethylene ketal to the 2'-lithio derivative which was then reacted with $[\text{PPh}_{3-n}\text{Cl}_n]$. The third method was a variation on this using a Grignard reagent instead of the organo-lithium compound with $[\text{PPh}_{3-n}\text{Cl}_n]$ and treating the resulting phosphanes with 4- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$ in acetone^[38] as shown in Scheme 3.2. The difficulty with these methods lay in the protection of the arylketone. Refluxing of 2'- $\text{BrC}_6\text{H}_4\text{COMe}$, $(\text{CH}_2\text{OH})_2$ and 4- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$ in toluene using a Dean-Stark trap for water gave better results than boron trifluoride etherate methods. The highest purity 2'-bromoacetophenone ethylene ketal obtained was not pure enough to continue with, given that the major impurity was the unprotected ketone.

The fourth method, used for this work, was a variation of the multi-step synthesis shown in Scheme 3.1 which started by coupling chlorodiphenylphosphane and 2-bromoethylbenzene. Subsequent oxidation of the phosphorus with H_2O_2 and of the ethyl group with KMnO_4 and MnO_2 in *conc*- HNO_3 at 40 °C were followed by reduction at the phosphorus atom.^[37] This route was closely adhered to in the above syntheses of $\text{Ph}_2\text{P}[\text{C}_6\text{H}_4\text{COMe}]$ except for the oxidation of the ethyl groups. It was not necessary to purify the 2-ethylphenyldiphenylphosphane before

proceeding with the hydrogen peroxide oxidation. In the attempted oxidation of $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{Et})$ to $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{COMe})$ with KMnO_4 and MnO_2 in *conc*- HNO_3 at either the 40 °C reported or at higher temperatures, $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{Et})$ was isolated in almost quantitative amounts in all cases. As no oxidation products were observed, more forcing conditions using CrO_3 in acetic acid were used.^[48] Initial investigations of oxidation using CrO_3 at 40 °C indicated that oxidation had indeed occurred, but a major product of $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{COOH})$ suggested over-oxidation. Also observed in minor quantities was the desired $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{COMe})$ along with small amounts of unreacted $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{Et})$ and $\text{Ph}_2\text{P}(\text{O})\text{OH}$. Oxidation with CrO_3 at lower temperatures, as used in this work, gave $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{COMe})$ as the major product. However, oxidation was not observed in all runs with no reaction at all in many cases. It has been found recently that an impurity in the acetic acid may have been the cause of this unpredictability, with the reaction proceeding reproducibly if the acetic acid is distilled from CrO_3 prior to carrying out the oxidation.^[49] The final reduction of P(V) to P(III) with Cl_3SiH proceeded smoothly to give $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$.

The effectiveness of this method in the preparation of $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$ led to attempts to prepare the analogous $\text{PhP}(\text{C}_6\text{H}_4\text{COMe})_2$ from PhPCl_2 and two equivalents of 2-bromoethylbenzene. This synthesis went as expected until the CrO_3 oxidation step, in which the product was $\text{PhP}[\overline{\text{C}_6\text{H}_4\text{COO}}]_2$, formed via what appeared to be $\text{PhP}(\text{O})(\text{C}_6\text{H}_4\text{COMe})(\text{C}_6\text{H}_4\text{Et})$; GC mass spectrum m/e 348 (M)⁺, 333 ($M - \text{Me}$)⁺, 305 ($M - \text{COMe}$)⁺, 290 ($M - \text{COMe} - \text{Me}$)⁺ and 243 ($M - \text{C}_6\text{H}_4\text{Et}$)⁺ (see Figure 3.13). The formation of $\text{PhP}[\overline{\text{C}_6\text{H}_4\text{COO}}]_2$ in the oxidation of $\text{PhP}(\text{O})(\text{C}_6\text{H}_4\text{Et})_2$ with CrO_3 in acetic acid is not surprising considering that the first time $\text{PhP}[\overline{\text{C}_6\text{H}_4\text{COO}}]_2$ was prepared it was by the acid

catalysed intramolecular dehydration of bis(*o*-carboxyphenyl)phenylphosphane oxide.^[40]

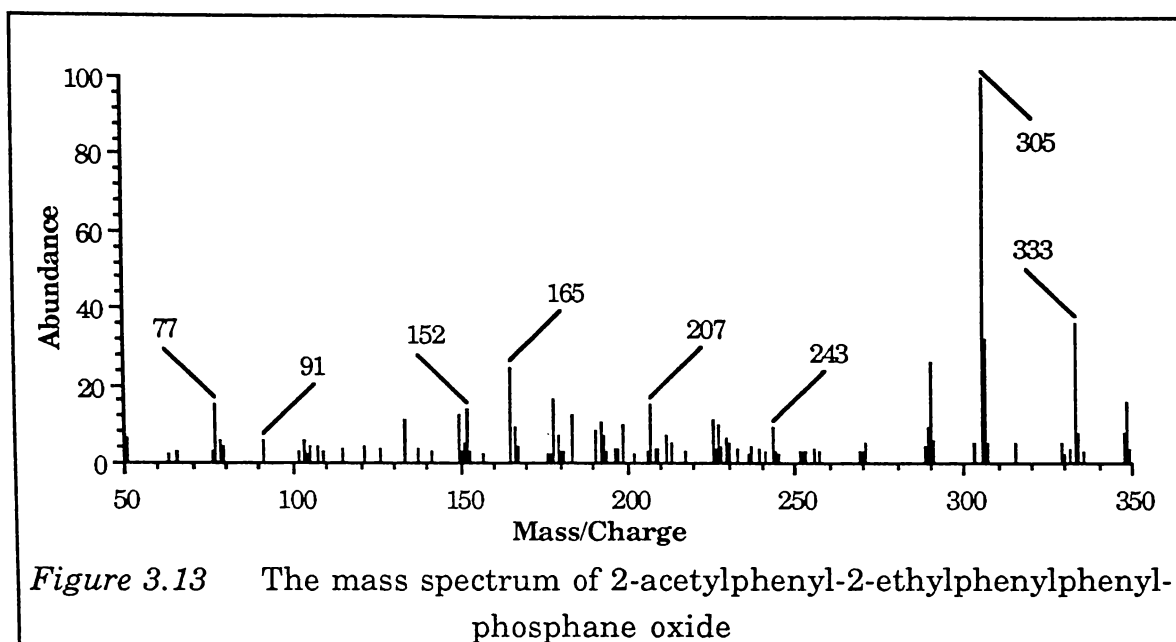


Figure 3.13 The mass spectrum of 2-acetylphenyl-2-ethylphenylphenylphosphane oxide

3.5 REACTION OF $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$ WITH $\text{Ru}_3(\text{CO})_{12}$

For the iron-group clusters $\text{M}_3(\text{CO})_{12}$ there are now good synthetic routes to substituted species $\text{M}_3(\text{CO})_{12-n}\text{L}_n$ ($n = 1$ to 4) for ruthenium and osmium using thermally-induced reactions, or by use of electron-transfer catalysts such as $[\text{Ph}_2\text{CO}]^{\cdot-}$ as initiators.^[50-52] Substitution reactions for the heavier element clusters can also be initiated using ionic salts such as $[\text{PPN}^+][\text{OAc}^-]$,^[53] by supported-metal catalysis using palladium on carbon,^[54,55] or by metal carbonyl dimers^[56-58] such as $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ or $[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\mu\text{-SMe})]_2$. For the reactions with uni-dentate and multi-dentate phosphane ligands the more predictable of these methods appears to be the lower temperature electron-transfer catalysis routes. For these methods when the ligand to metal-carbonyl ratio is maintained around 1:1 the main product, in the majority of cases, is the simple mono-substituted $\text{M}_3(\text{CO})_{11}\text{L}$ species.^[50,51]

The good product selectivity and reasonable yields obtained from the above electron-transfer catalysis (ETC) reactions suggest that this

would be the method of choice for introducing $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$ into a metal cluster for subsequent reaction.

As discussed in Section 3.1 the phosphane $\text{Ph}_2\text{P}(2\text{-C}_6\text{H}_4\text{CH=CH}_2)$ (sp) was shown to be the alkene equivalent of a β -ketophosphane, hence one might expect similar reactivities. It has been shown that the ETC reaction of $\text{Ru}_3(\text{CO})_{12}$ with sp in a 2:1 ratio gives $\text{Ru}_3(\text{CO})_{10}(\text{sp})$ in which two *cis* equatorial positions on adjacent ruthenium atoms are displaced by the chelate ligand. The sp ligand in $\text{Ru}_3(\text{CO})_{10}(\text{sp})$ is found to bridge one of the Ru-Ru bonds with the phosphorus atom bonded to one ruthenium and the vinyl group bonded to the other as an η^2 -group. On pyrolysis $\text{Ru}_3(\text{CO})_{10}(\text{sp})$ undergoes ready migration of hydrogen from the η^2 -olefin to the metal cluster, with concomitant loss of CO and structural rearrangement to give a μ_3 - η^2 -alkyne cluster, $\text{H}_2\text{Ru}_3(\text{CO})_8(\mu_3\text{-HCCC}_6\text{H}_4\text{PPh}_2)$.^[33]

3.5.1 Experimental

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen although subsequent work-up was carried out with no precaution to exclude air. The sodium diphenylketyl solution was prepared as discussed Chapter One.

3.5.2 Preparation of $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$

A stirred solution of $\text{Ru}_3(\text{CO})_{12}$ (1) (0.100 g, 0.156 mmol) and $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$ (0.047 g, 0.155 mmol) in THF (30 ml) was treated dropwise with a solution of $[\text{Ph}_2\text{CO}]^-$ in THF (ca. 1 ml) until the solution turned dark red and the 2061 cm^{-1} band of $\text{Ru}_3(\text{CO})_{12}$ was absent, as shown by infrared spectroscopy. Solvent was removed and the residue dissolved in a minimum of dichloromethane. PLC (silica gel) using 40-60°C petroleum spirits/dichloromethane (1:1) eluent gave seven products: (i) $\text{Ru}_3(\text{CO})_{12}$ (0.0081 g, 8 %); (ii) orange $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ (2), (trace) identified from its infrared spectrum (see below); (iii) orange

Table 3.6 Reaction products from the reaction between $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$.				
Band	Colour	R_f	Yield g (%)	Product
1	Yellow	0.98	0.0081 (8)	$\text{Ru}_3(\text{CO})_{12}$
2	Light Orange	0.95	trace	$\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$
3	Orange	0.61	0.0696 (49)	$\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$
4	Light Orange	0.49	trace	(U1)
5	Yellow	0.25	trace	-
6	Yellow	0.09	trace	-
7	Yellow-Brown	0.00	trace	(U2)

solid, characterised as $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$ (**3**), $\nu(\text{CO})_{\text{hexane}}$ (2099 m, 2082 vw, 2046 s, 2033 m, 2030 m, 2016 vs, 1998 w, 1987 vw and 1982 vw) cm^{-1} (see Section 3.5.2.1), FAB mass spectrum m/e 917 (M)⁺ and a succession of carbonyl fragment (m/e 28) losses down to m/e 609 ($M - 11\text{CO}$)⁺ (see Section 3.5.2.2), ^{13}C nmr (δ 29.7 q -C(O)CH₃), ^{31}P nmr (δ 40.1 s). Four other products were also present in trace amounts. Two of these were not investigated further. The third compound (U1) is recorded as band 4 in Table 3.6 and has the infrared spectrum $\nu(\text{CO})_{\text{hexane}}$ (2086 vw, 2067 s, 2061 s, 2059 vw sh, 2049 w, 2032 w sh, 2026 s, 2020 s, 2013 w sh, 1996 vw, 1989 m and 1963 w) cm^{-1} and the FAB mass spectrum of m/e 1083, 1027, 971, 878, 869, 803, 794, 775, 766, 747, 738, 719 and 710. The fourth unidentified product (U2), obtained in trace amounts from band seven by washing the silica gel with acetone, has the infrared spectrum $\nu(\text{CO})_{\text{CH}_2\text{Cl}_2}$ (2090 vw, 2060 s, 2048 w sh, 2023 m sh, 2003 s, and 1989 m sh) cm^{-1} .

3.5.2.1 Vibrational spectroscopy of $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$

The infrared spectrum of (**3**) in the carbonyl region was recorded in hexane, CH_2Cl_2 and as a KBr disc (Figure 3.14). The position and intensities of bands in the solution phase $\nu(\text{CO})$ spectra of (**3**) are very

similar to those found for other mono-substituted $\text{Ru}_3(\text{CO})_{12}$ clusters such as $\text{Ru}_3(\text{CO})_{11}(\text{PMe}_2\text{Ph})^{[52]}$ as shown in Table 3.7. This combined with the method of preparation, the FAB mass spectrum and the thermolysis products strongly favour the formulation of (3) to be, as previously stated,

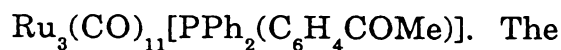


Table 3.7 Comparison of the hexane solution phase infrared spectra of $\text{Ru}_3(\text{CO})_{11}\text{L}$ clusters.			
L = $\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})$		L = PMe_2Ph	
2099	m	2096	m
2046	s	2044	s
2033	m		
2030	m	2028	s
2016	vs	2016	s
1998	w	2000	w
1987	vw	1987	w

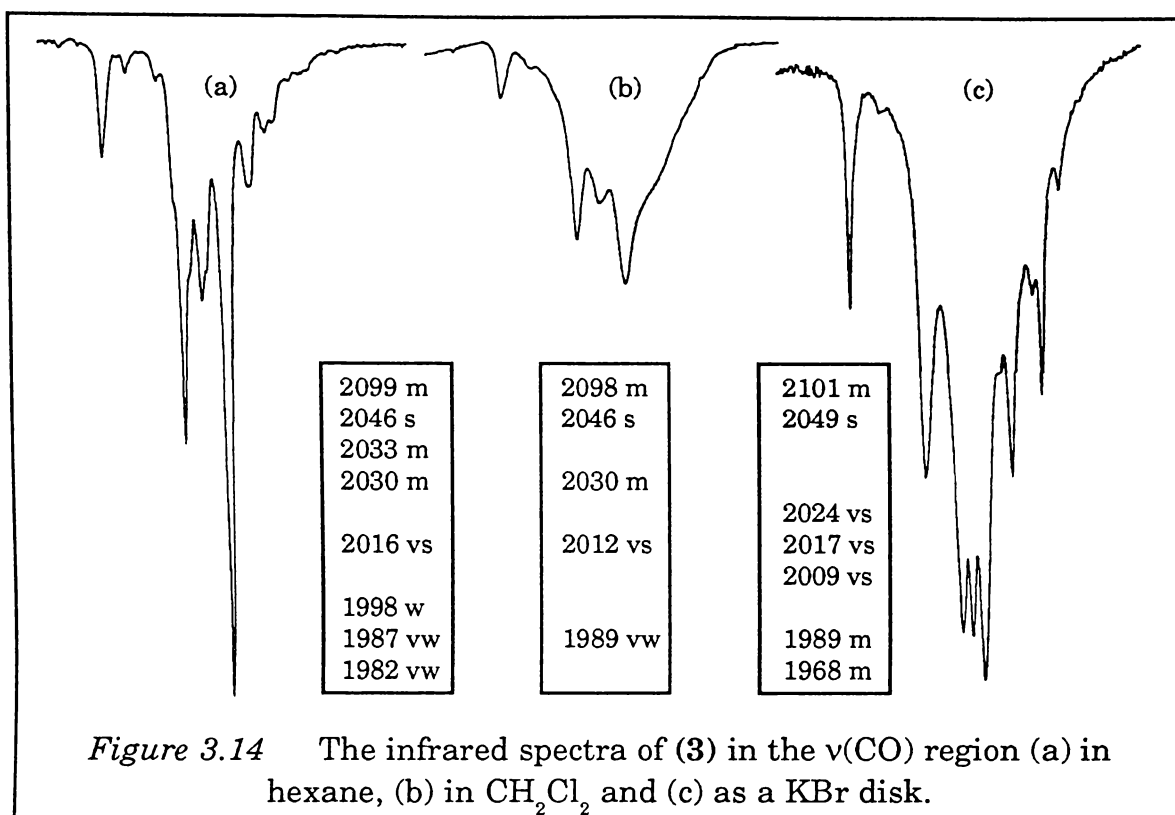
stretching frequency for the ketone function on the phosphane ligand, which is observed as a broad band centred at 1632 cm^{-1} is shifted to lower energy compared to the two mono-nuclear manganese complexes $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{-}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$ (R = H or Me) (1690 cm^{-1})^[36] and the free ligand

(1670 cm^{-1}). However it is markedly higher in energy than those found for *cyclo*-manganated complexes of aromatic ketones^[60,61] where coordination lowers the frequency by about 150 cm^{-1} compared to the free ligand. The relatively small difference in energy for the carbonyl vibration of (1) and free acetophenone can probably be explained by a slight change in coupling to the phenyl ring C-C stretches.

3.5.2.2 FAB mass spectrum of $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$

The FAB mass spectrum of $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$, shown in Table 3.10, is consistent with the formulation, showing a molecular ion M^+ with m/e 917 and a succession of carbonyl fragment (m/e 28) losses down to a m/e of 609 ($\text{Ru}_3[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]^+$). Two other series are observed involving the loss of successive carbonyl fragments. The first begins at m/e 619 ($\text{Ru}_2(\text{CO})_4[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]^+$) and ends with the loss of all carbonyl ligands at m/e 507; the second is a series of fragment ions

which contain only one ruthenium atom, beginning at m/e 462 ($\text{Ru}(\text{CO})_2[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]^+$) and ending at m/e 406.



3.5.3 Preparation of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$

A stirred solution of (3) (0.190 g, 0.208 mmol) in n-heptane (70 ml) was heated at 60°C until the solution turned green and the 2016 cm^{-1} band of (3) was absent as shown by infrared spectroscopy. The reaction was generally complete within 4 hours. Solvent was removed and the residue dissolved in a minimum of dichloromethane. PLC (silica gel) using $30\text{-}40^\circ\text{C}$ petroleum spirits/dichloromethane (3:1) eluent gave six products: (i) $\text{Ru}_3(\text{CO})_{12}$ (1) (0.0633 g, 48 %); (ii) pale yellow (trace); (iii) green (trace); (iv) orange characterised as $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ (2) (0.0818 g, 44 %) by a full X-ray crystal structure determination (see Section 3.6), $\nu(\text{CO})_{\text{hexane}}$ (2099 m, 2059 m, 2027 vs, 1999 w, 1992 m, 1984 m, 1952 w and 1855 w br) cm^{-1} (see Section 3.5.3.1), its FAB mass spectrum m/e 861 ($M - \text{CO}$) $^+$ and a succession of carbonyl fragment (m/e 28) losses down to m/e 609 ($M - 10\text{CO}$) $^+$ (see Section 3.5.3.2); (v) yellow (trace); (vi)

Table 3.8 Products from the thermolysis of $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$.					
Product	Colour	40°C		60°C	
		R_f	Yield g (%)	R_f	Yield g (%)
(1)	Yellow	0.99	0.0096 (30)	0.99	0.0633 (48)
(U4)	Light Orange	0.95	0.0096		
(U5)	Yellow	0.91	0.0024	0.56	0.0091
(U6)	Green	0.85	0.0042	0.43	trace
(2)	Orange	0.79	0.0098 (22)	0.39	0.0818 (44)
	Brown	0.66	trace		
(U7)	Yellow	0.51	trace	0.20	0.0080
(U3)	Orange-Brown	0.00	0.0021	0.00	trace

orange-brown (trace). Bands (ii), (iii), (v) and (vi) were not investigated further.

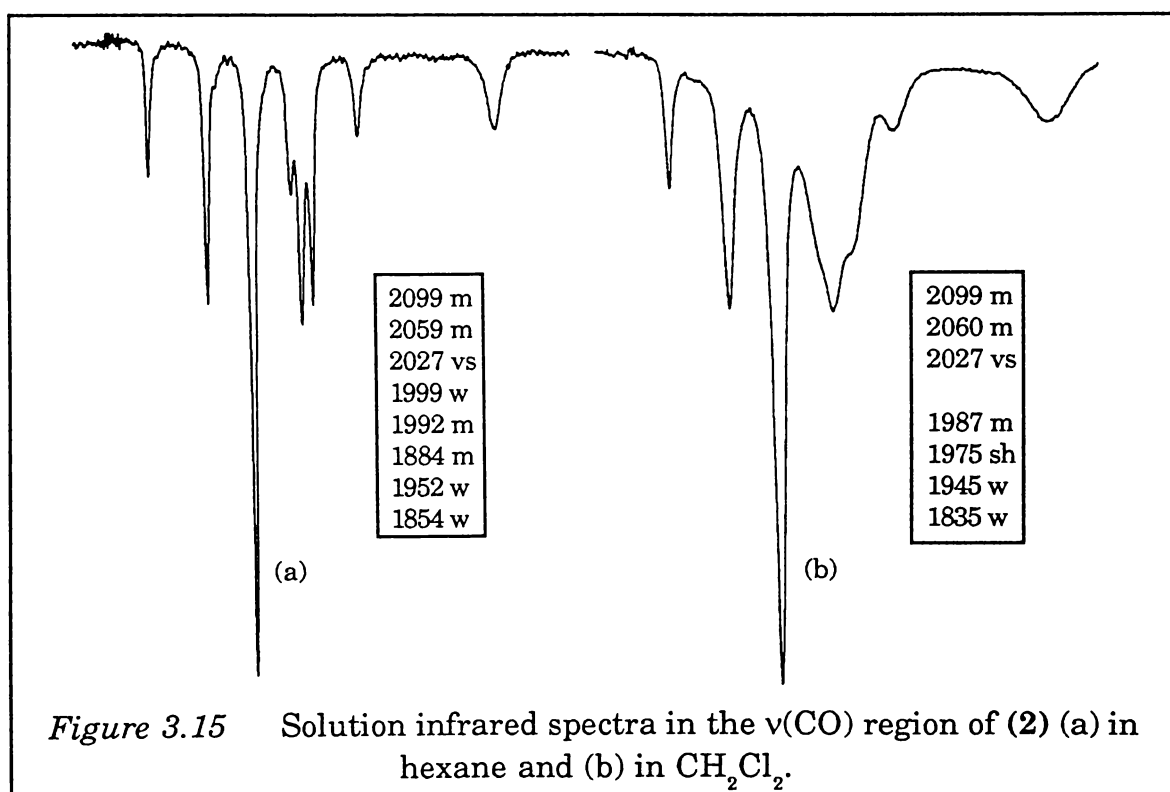
The thermolysis of (3) in heptane was carried out at different temperatures in an attempt to improve the yield of (2). The ratio of products (1):(2) was found to be approximately 1:1 for all the temperatures used. The results for the thermolysis at 40°C are summarised in Table 3.8, while for the 27°C reaction 50 % of (3) had reacted to give (1) and (2) after 2 days. The 40°C reaction was carried out as for the 60°C reaction above with the following differences: (3) (0.046 g, 0.050 mmol) in n-heptane (20 ml); complete reaction required 4.75 days to give a green solution and a brown precipitate; a 30-40°C petroleum spirits/dichloromethane ratio of (2:1) was used for the eluent; the brown residue (U3) was soluble in CH_2Cl_2 to give two infrared bands in the carbonyl region, $\nu(\text{CO})_{\text{CH}_2\text{Cl}_2}$ (2046 m and 1974 m) cm^{-1} . The simplicity of this spectrum suggests a mono-nuclear dicarbonyl species.

The temperature of choice for the thermolysis of (3) to give (2) in heptane was found to be 60°C. At this temperature the number and quantities of minor products formed was smallest. (1) was the major

product at 60°C, but this was found to be the case at all temperatures tried. The fate of the phosphane ligand in the formation of (1) is unknown. Some of it may be associated with the unknown compounds in the form of diphosphane complexes. However this would not account for all of it considering the large amounts of (1) isolated. The identification of band one as (1) was based solely on infrared analysis of the product in the $\nu(\text{CO})$ region. The pale-yellow colour of the free phosphane gives it a similar appearance to (1). Hence band one may have been a mixture of the free phosphane and (1).

3.5.3.1 Vibrational spectroscopy of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$

The solution infrared spectra of (2) in the $\nu(\text{CO})$ region were recorded in hexane and CH_2Cl_2 (see Figure 3.15). The two spectra are very similar with the usual broadening of bands in the more polar solvent. Comparison of the spectra with other tri-substituted $\text{Ru}_3(\text{CO})_{12}$ clusters shows some similarity. These clusters generally have a weak to medium intensity band between 2050 and 2085 cm^{-1} ,¹ an envelope of up to three



medium to strong, broad absorptions in the 2050-1975 cm^{-1} region and another weak band around 1950 cm^{-1} . Of the three central bands, the central one of these three is generally the strongest and in many cases the lower energy band of the three has one or two shoulder bands. Cluster (2) conforms to this pattern with the additional absorption at 1835 cm^{-1} indicating the presence of a bridging carbonyl ligand in solution. The central, most intense band for (2) occurs at higher energy than for the clusters $\text{Ru}_3(\text{CO})_9\text{L}_3$ ($\text{L} = \text{PMe}_3$, $\text{P}(\text{OMe})_2\text{Ph}$)^[52]. This indicates the lower basicity of $(\mu\text{-PPh}_2)$ and $(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ as compared to PMe_3 and $\text{P}(\text{OMe})_2\text{Ph}$.

3.5.3.2 FAB mass spectrum of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$

The FAB mass spectrum of (2), shown in Table 3.10, is consistent with the formulation as determined by X-ray structure analysis. The parent ion is observed with the highest m/e of 861 corresponding to $(\text{M})^+$. As for (3) there is a succession of carbonyl fragment (m/e 28) losses from the highest mass down to m/e 609 ($\text{M} - 9\text{CO}$)⁺ corresponding to the fragment ion $[\text{C}_{20}\text{H}_{20}\text{OPRu}_3]^+$.

3.5.3.3 Analysis of the Ru_n clusters

The infrared spectral data of the unknown clusters reported above are given in Table 3.9, the spectra in Figure 3.16 and FAB mass spectral assignments in Table 3.10. Three of these clusters have spectra similar to known clusters: the spectra of (U2), (U4) and (U5) in hexane are consistent with a $\text{Ru}_3(\text{CO})_9\text{L}_3$ species, $\text{Ru}_3(\text{CO})_{11}\text{L}$ and $\text{Ru}_3(\text{CO})_{11}\text{L}$ species^[52] respectively. The FAB mass spectra for (U4) and (U5) are consistent with these formulations, with the highest recorded ion being m/e 861 ($\text{Ru}_3(\text{CO})_9\text{L}$; $\text{L} = \text{Ph}_2\text{PC}_6\text{H}_4\text{COMe}$) in both cases, but they do not exclude higher substitution patterns.

The isotope patterns, fragment ions and molecular ions for (2), (3), (U4), (U5) and (U6) are all consistent with the formulation of these as Ru_3 species with at least nine carbonyl ligands and all the substituent atoms of one $\text{Ph}_2\text{PC}_6\text{H}_4\text{COMe}$ group. All of these clusters show fragment ions belonging to one or more of three main breakdown series, which involve one, two or three ruthenium atoms ($\text{Ru}(\text{CO})_n\text{L}$ $n = 0-2$; $\text{Ru}_2(\text{CO})_n\text{L}$ $n = 0-4$; $\text{Ru}_3(\text{CO})_3\text{L}$ $n = 0-11$).

Table 3.9 Infrared spectra of the unidentified ruthenium clusters.							
(U1)		(U2)	(U4)		(U5)	(U6)	
hexane	CH_2Cl_2	CH_2Cl_2	hexane	CH_2Cl_2	hexane	hexane	CH_2Cl_2
2086 vw		2090 vw	2097 w	2097 w	2097 s	2100 m	2099 m
2067 s	2069 s		2087 s	2086 m	2088 vw	2084 m	2083 w
2061 s	2060 s	2060 s			2062 w		
2059 vw						2057 vs	2055 vs
2049 w	2048 w	2048 w	2049 vs	2048 vs	2049 w	2051 w	
						2040 w	
2032 w			2030 w	2029 w	2030 vs	2031 s	
2026 s						2028 s	2027 vs
2020 s	2023 vs	2023 m	2023 vw		2024 vs	2023 m	
			2017 s	2112 vw		2017 vw	
2013 w			2010 vs		2009 vs		
		2003 s		2005 vs		2004 vw	
1996 vw			1998 m			1999 s	
1989 m		1989 m	1983 w		1991 m	1991 vw	1989 s
				1977 vw		1972 w	
1963 w			1962 m				
			1955 vw	1952 w	1955 s		

The cluster (U1) varies from the above pattern in that it exhibits a fragment ion of m/e 1083 with isotopic ratios consistent with Ru_4 as the central core of metal atoms. While the mass spectrum (U1) has some fragments belonging to the above $\text{Ru}_3(\text{CO})_3\text{L}$ series, the majority of the fragments contain four ruthenium atoms and they belong to either the

$\text{Ru}_4(\text{CO})_n(\text{Ph}_2\text{PC}_6\text{H}_4\text{COMe})(\text{C}_6\text{H}_4\text{COMe})$ ($n = 0-9$) or the $\text{Ru}_4(\text{CO})_n(\text{Ph}_2\text{PC}_6\text{H}_4\text{COMe})$ ($n = 0-6$) series.

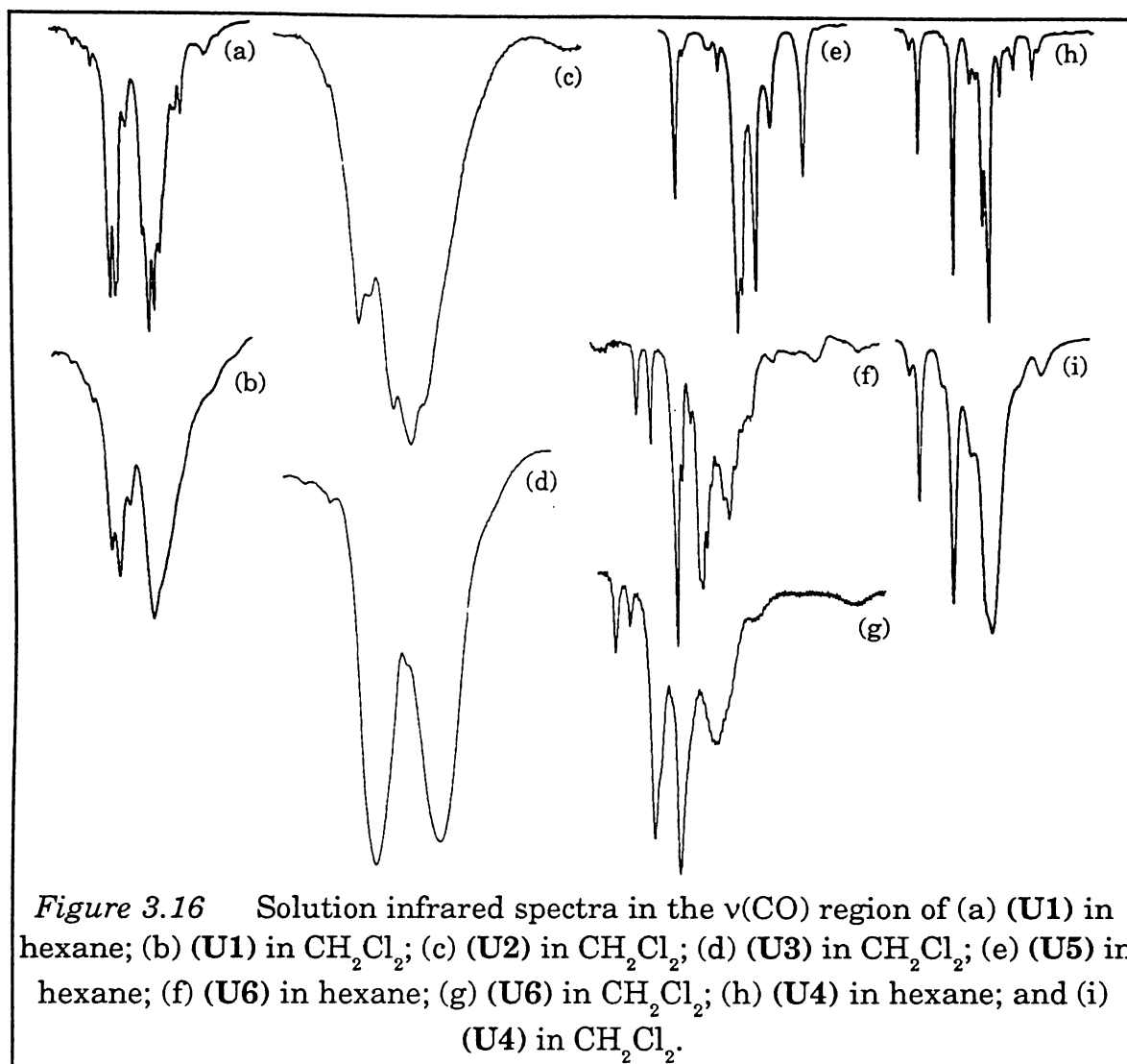


Table 3.10 Mass spectral assignment of the ruthenium clusters.

Breakdown Series [#]	Values for n					
	(2)	(3)	(U1)	(U4)	(U5)	(U6)
$\text{Ru}_4(\text{CO})_n\text{L}(\text{C}_6\text{H}_4\text{COMe})$	-	-	1,5,7,9	-	-	-
$\text{Ru}_4(\text{CO})_n\text{L}$	-	-	0-3,6	-	-	-
$\text{Ru}_3(\text{CO})_n\text{L}$	0-9	0-8, 10,11	4,5,6,7	2-9	5-9	0-7,9
$\text{Ru}_2(\text{CO})_n\text{L}$	2,3,4	0-4	-	-	0-4	-
$\text{Ru}(\text{CO})_n\text{L}$	-	0-2	-	-	-	-
[#] L = $(\text{Ph}_2\text{PC}_6\text{H}_4\text{COMe})$						

3.6 $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$, AN X-RAY CRYSTALLOGRAPHIC STUDY

3.6.1 Data Collection

Orange, wedge shaped crystals of (2) were grown from a solution of (2) in n-heptane, which had been cooled from room temperature to -20°C for two days.

One of the well-formed crystals was attached to a fine glass fibre with grease and mounted on a goniometer. Preliminary precession photography indicated a triclinic unit cell with space group of $P1$ or $P\bar{1}$.

A crystal, of dimensions $0.40 \times 0.20 \times 0.10$ mm, was sent to the University of Canterbury for intensity data collection. Using a Nicolet P3 diffractometer with zirconium filtered Mo-K_α radiation, a total of 4362 unique reflections were collected within the range of $4^\circ < 2\theta < 45^\circ$. Data were collected in $P\bar{1}$ with $a = 10.200(11)$, $b = 12.084(12)$ and $c = 14.422(13)$ Å, $\alpha = 81.06(7)$, $\beta = 77.18(8)$ and $\gamma = 76.98(8)^\circ$; $U = 1678(3)\text{Å}^3$ and $Z = 2$. The crystal data are given in Table 3.11.

Corrections were made for Lorentz and polarisation effects, together with an empirical absorption correction which gave transmission factors ranging from 0.976 to 0.695. All reflections with $I < 0.5\sigma$ were replaced by 0.25σ . This left 2732 reflections with $I > 2.0\sigma(I)$ which were used in all the calculations.

3.6.2 Solution and Refinement

The structure was solved using the TREF direct method routine of SHELXS86.^[39] This revealed the three ruthenium atoms, the phosphorus atom and a few of the carbon and oxygen atoms. Subsequent refinement and difference-map cycles revealed the remaining carbonyl ligands and n-heptane of crystallisation. All non-hydrogen atoms except for the

C_7H_{16} molecule per unit cell. The disorder is such that the unit cell appears to contain an octane molecule. Half occupancy of the carbon sites at each end of the carbon chain gives the disordered C_7H_{16} molecule. These atoms also had significant ellipsoidal contributions to their thermal parameters. Due to the “floppy-ness” of the carbon atoms of the half n-heptane molecule, no attached hydrogen atoms were included in the final refinement cycle.

The final difference map showed some residual electron density of *ca.* $1.0 e \text{ \AA}^{-3}$ near ring 5, one of the isotropic phenyl rings. This can be attributed to difficulties with absorption corrections and the rigid constraints applied to this phenyl ring in the final refinement cycles. No parameter shifted by more than two percent of its estimated standard deviation in the final refinement cycle, with the largest shift of 1.7 % found for the x-rotation of ring 5.

Table 3.12 Selected bond lengths and angles for
 $Ru_3(CO)_9(\mu-PPh_2)(\eta^2-C_6H_4COMe)\cdot\frac{1}{2}C_7H_{16}$.

Bond Lengths (pm)

Ru(1)---Ru(2)	283.6(2)	Ru(3)---C(41)	207.9(14)
Ru(1)---Ru(3)	294.7(2)	Ru(3)---O(47)	212.2(10)
Ru(2)---Ru(3)	292.6(2)	C(41)---C(42)	136.6(20)
Ru(1)---C(14)	220.2(14)	C(42)---C(47)	147.2(20)
Ru(2)---C(14)	202.1(16)	C(47)---O(47)	123.3(17)
Ru(1)---P(1)	233.9(4)	C(71)---C'(71)	152.6(37)
Ru(3)---P(1)	232.8(4)	C(71)---C(72)	149.5(24)
P(1)---C(51)	183.1(7)	C(72)---C(73)	154.2(25)
P(1)---C(61)	181.3(9)	C(73)---C(74)	124.3(39)
C(Ph)---C(Ph)	136.6(20)-143.1(19)		

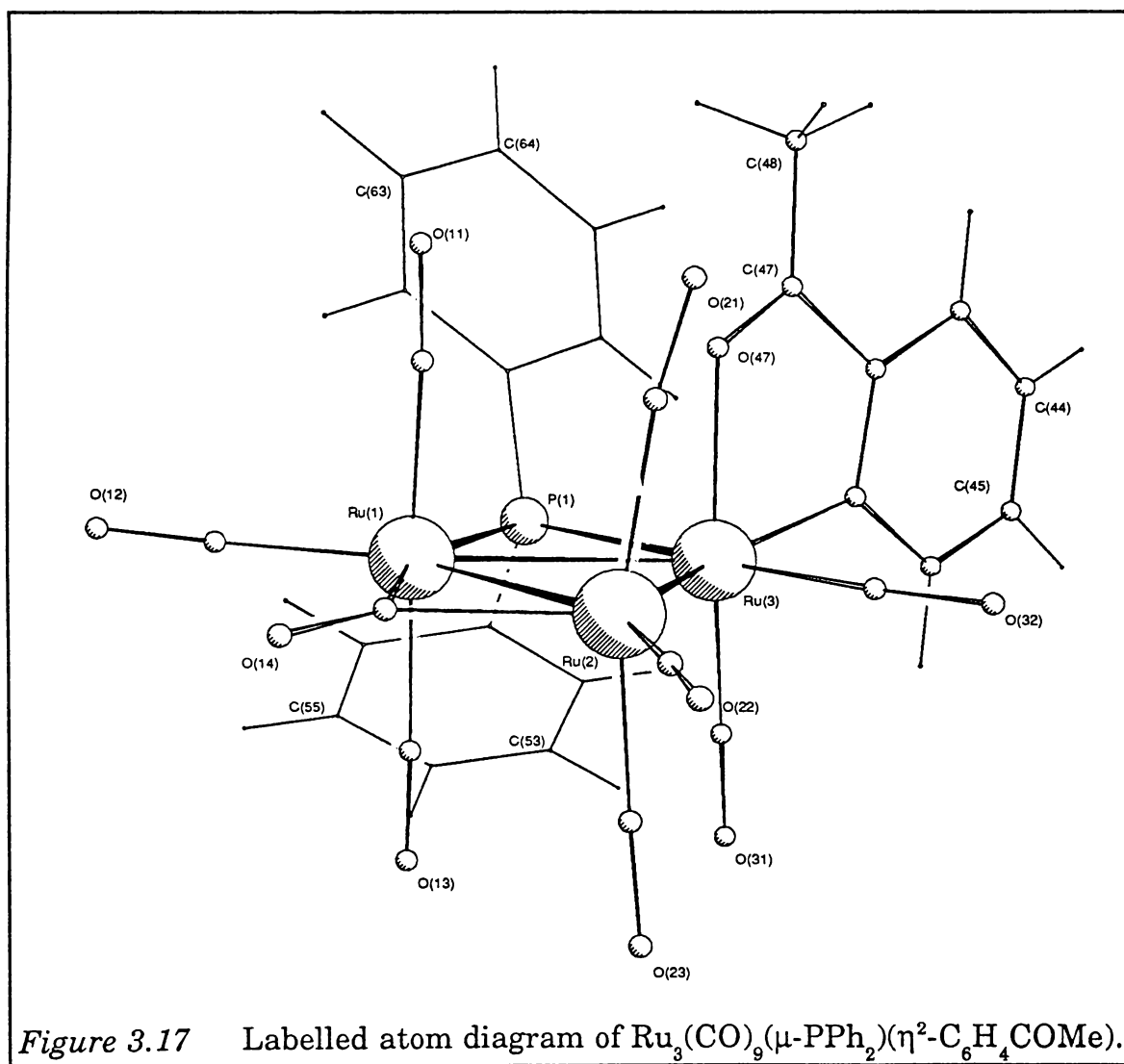
Bond Angles (°)

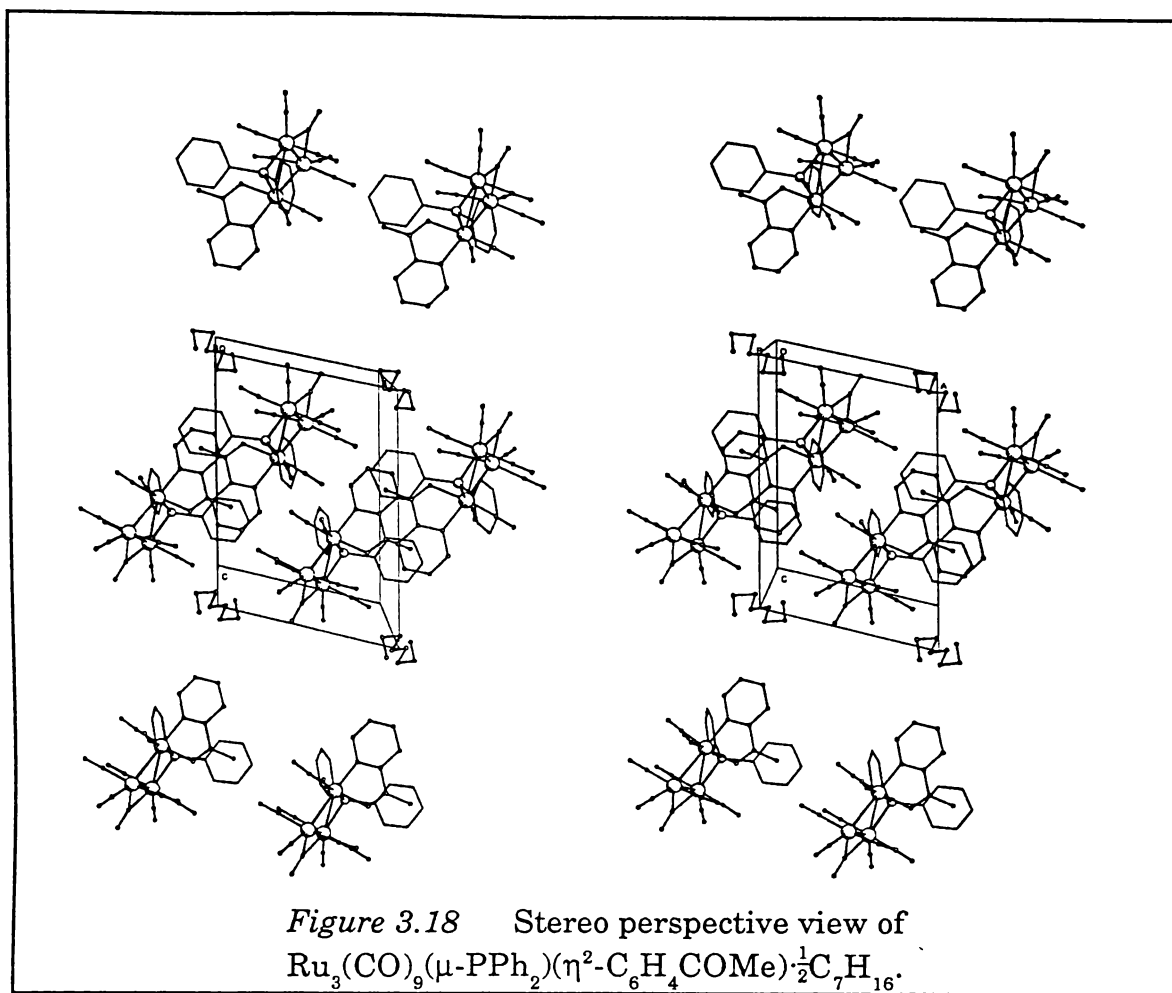
Ru(2)-Ru(1)-Ru(3)	60.8(0)	Ru(3)-C(41)-C(42)	113.0(10)
Ru(1)-Ru(2)-Ru(3)	61.5(0)	C(41)-C(42)-C(47)	116.1(14)
Ru(1)-Ru(3)-Ru(2)	57.7(0)	C(42)-C(47)-O(47)	116.7(14)
C(41)-Ru(3)-O(47)	77.6(5)	C(47)-O(47)-Ru(3)	116.3(9)
C(Ph)-C(Ph)-C(Ph)	116.8(14)	C(7n)-C(7n)-C(7n)	113.2(17)
	-122.9(14)		-113.4(26)

Selected bond lengths and angles are given in Table 3.12, while all bond lengths and angles, the final positional parameters and final thermal parameters are in Appendix 3.

3.6.3 Discussion of the Structure of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$

The structure of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ consists of discrete molecules. A labelled atom diagram of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ is shown in Figure 3.17 and a stereo view showing the relationship between the $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ molecule and the n-heptane molecule of crystallisation is shown in Figure 3.18.





The overall geometry of (2) consists of a central triangle of ruthenium atoms. Bonded to these central atoms are one PPh_2 moiety bridging the $\text{Ru}(2)\text{-Ru}(3)$ bond, one chelating $\text{C}_6\text{H}_4\text{COMe}$ group bonded to $\text{Ru}(3)$ and nine carbonyl ligands. Eight of the carbonyl ligands are terminal (three bonded to $\text{Ru}(1)$, three to $\text{Ru}(2)$ and two to $\text{Ru}(3)$) and the remaining carbonyl bridges the $\text{Ru}(1)\text{-Ru}(2)$ bond. This results in one pseudo-octahedral ruthenium atom ($\text{Ru}(1)$) and two seven coordinate, distorted pentagonal bipyramidal ruthenium atoms ($\text{Ru}(2)$ and $\text{Ru}(3)$). The axial sites on $\text{Ru}(2)$ and $\text{Ru}(3)$ are filled by three carbonyl ligands and the oxygen atom of the chelating $\text{C}_6\text{H}_4\text{COMe}$ group.

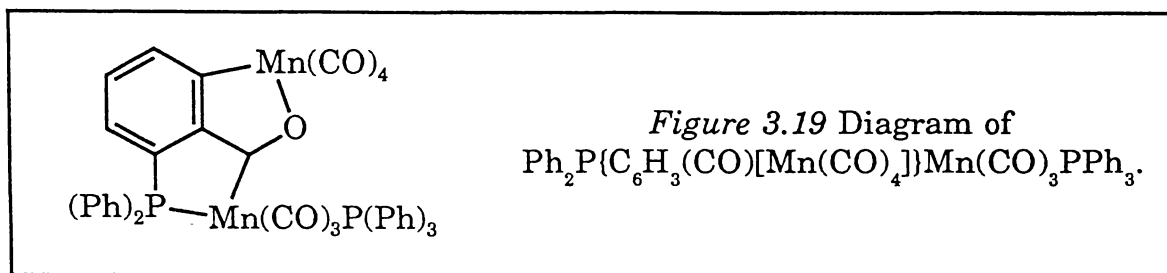
The geometry of the ligands in the plane of the ruthenium atoms is by no means regular. This is shown by the large $\text{Ru}(3)\text{-Ru}(2)\text{-C}(22)$, $\text{C}(22)\text{-Ru}(2)\text{-C}(14)$, $\text{C}(14)\text{-Ru}(1)\text{-C}(12)$, $\text{C}(12)\text{-Ru}(1)\text{-P}(1)$, $\text{P}(1)\text{-Ru}(3)\text{-C}(41)$ and

C(41)-Ru(3)-C(32) angles. Near equilateral geometry of the central Ru_3 triangle is indicated by the Ru-Ru-Ru bond angles (60.8, 61.5 and 57.7 °) being close to the ideal value of 60 ° and the similar bond distances (range 283.6 to 294.7 pm). These distances (290.3_{av} pm) while marginally longer than those found in $\text{Ru}_3(\text{CO})_{12}$ (285.1 pm)^[62], $\text{Ru}_3(\text{CO})_{10}(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (285.3_{av} pm)^[63] and $\text{Ru}_3(\text{CO})_{10}(\text{Ph}_2\text{PC}_6\text{H}_4\text{CHCH}_2)$ (285.3_{av} pm)^[33] are not significantly different from Ru-Ru bond distances found in the clusters $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$ (288_{av} pm)^[64] and $\text{H}_2\text{Ru}_3(\mu_3\text{-HCCC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$ (287.5_{av} pm)^[33]. The shortest Ru(1)-Ru(2) bond distance of 283.6 pm is associated with the bridging carbonyl group. This shortening of the carbonyl-bridged bond is common in cluster chemistry. The $\mu\text{-(CO)}$ group does not symmetrically bridge the Ru(1)-Ru(2) bond. The Ru(1)-C(14) and Ru(2)-C(14) bond distances of 220(1) and 202(2) pm respectively show that the carbon atom is displaced towards Ru(2). In contrast to this the $\mu\text{-PPh}_2$ moiety bridges the Ru(1)-Ru(3) bond symmetrically, with Ru(1) and Ru(3) to P(1) bond distances of 233.9(4) and 232.8(4) respectively. These Ru-P distances are similar to those found for $\mu\text{-PPh}_2$ ligands found in other ruthenium clusters: 234.1_{av} pm found for $\text{Ru}_3(\text{CO})_8(\text{C}_2\text{Bu}^t)(\text{PPh}_2)$;^[65] 230.2_{av} pm for $\text{Ru}_2(\text{NO})_2(\text{PPh}_3)_2(\mu\text{-PPh}_2)$.^[66] The phosphorus atom is essentially co-planar with the three ruthenium atoms, with no atom deviating from the least square plane by more than 1 pm. The equatorial, terminal carbonyl ligand attached to Ru(3) is displaced somewhat towards Ru(2), possibly due to steric interactions in the metal plane around Ru(3) between the phenyl group of the chelating $\text{-C}_6\text{H}_4\text{C(OMe)}$ group and the phosphorus atom of the bridging PPh_2 moiety. This displacement gives a Ru(1)···C(32) non-bonding distance of 273 pm. The remaining Ru-C distances (range 184(2) to 195(2) pm), the carbonyl ligand C-O bond distances (range 114(2) to 119(2) pm) and the P-C bond distances (182_{av} pm) are normal. The 48 bonding electrons in this cluster (6 from each Ru, 2 from each CO, 3 from

the bridging P and 3 from the acetophenone ligand) is the same as found in the parent cluster $\text{Ru}_3(\text{CO})_{12}$ (6 from each Ru and 2 from each CO ligand).

The chelating $\text{—C}_6\text{H}_4\text{COMe}$ group is bonded to Ru(3) through the *ortho*-carbon atom on the phenyl ring and the oxygen atom of the ketone residue. The oxygen atom occupies an axial site on the ruthenium atom as would be expected for the more electronegative ligand. The $\text{—C}_6\text{H}_4\text{COMe}$ group, which is approximately planar with a largest deviation from the least square plane being 3 pm, is almost perpendicular to the Ru_3 plane (dihedral angle of 85.2°). The C-C bond lengths (range 136.6(20) to 143.1(19) pm) and C-C-C bond angles (range $116.8(14)$ to $122.9(14)^\circ$) within the phenyl ring of the $\text{C}_6\text{H}_4\text{COMe}$ residue are consistent with sp^2 -hybridised carbon atoms. The shortest bond distance is along the C(41)-C(42) bond which is contained within both the phenyl ring and the five membered C—O—Ru—C—C ring. The C(42)-C(47) bond length of 147(2) pm is consistent with single bonds between sp^2 -hybridised carbon atoms (the analogous bond in free acetophenone is 149.4 pm^[67]). This indicates little or no electron delocalisation within the five-membered C—O—Ru—C—C ring. The C(47)-O(47) bond length of 123(2) pm, compared to 127 pm for the manganese cluster $\text{Ph}_2\text{P}\{\text{C}_6\text{H}_3(\text{CO})[\text{Mn}(\text{CO})_4]\}\text{Mn}(\text{CO})_3\text{PPh}_3$ ^[68] (see Figure 3.19), 124 pm for 2-MeC(O) $\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$ in which delocalisation is indicated^[69] and 121.6(2) pm for free acetophenone, is normal for an sp^2 -carbon to sp^2 -oxygen double bond. This also precludes delocalisation, as do the Ru(3)-C(41) and Ru(3)-O(47) bond lengths within the ring. These distances of 208(1) and 212(1) pm are comparable to the analogous single bond distances found for other ruthenium complexes. For example in the mono-nuclear cluster $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\eta^2\text{-2-C}_6\text{H}_4\text{COMe})$ ^[70] the bond distances are 207(2) and 212.5(8) pm respectively; for carboxylate complexes such as $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\eta^2\text{-O(O)CMe})$ and

$\text{RuCl}_2(\text{PPh}_3)_2(\eta^2\text{-OOCPh})$ Ru-O single bond distances of 213(1)^[71] and 211.8(1) pm^[72] are observed. Similarly the Ru-C bond falls within the range of known Ru-C(*sp*²) distances (196(1) to 216(1) pm)^[73,74]



In the n-heptane molecule of crystallisation the C-C bond lengths (range 150(2) to 154(3) pm), excluding the C(73)-C(74) bond, are normal for *sp*³-carbon to *sp*³-carbon single bonds. The very short C(73)-C(74) bond of 124(2) pm is probably an artefact produced by the high anisotropy of the terminal, disordered carbon atom, C(74). The normal C-C-C bond angles of 113_{av}° give rise to a spiralling carbon chain with a sense change at the inversion centre.

3.7 DISCUSSION OF THE REACTION OF $\text{PPh}_2(2\text{-C}_6\text{H}_4\text{COMe})$

The electron-transfer catalysed reaction of $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$ with $\text{Ru}_3(\text{CO})_{12}$ in an 1:1 ratio gave the expected cluster, $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$ (**3**), in good yields. Although not identified by X-ray crystallography, (**3**) was characterised by mass spectral analysis and comparison of the solution phase infrared spectrum with analogous clusters such as $\text{Ru}_3(\text{CO})_{11}(\text{PMe}_2\text{Ph})$. The $\nu(\text{C}=\text{O})$, while found at lower energy than for the free ligand and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2[\text{PPh}_2(\text{C}_6\text{H}_4\text{COMe})]$, is higher in energy than those observed for η^2 -manganese complexes.

Thermally induced reaction of the cluster (**3**), discussed above, led to the formation of $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$ (**2**) via P-C bond cleavage. While oxidative addition of a P-C bond in pyrolysis reactions of Ru_3 phosphane clusters in itself is not unusual, retention of the Ru_3 core in the process is less common. In the majority of pyrolysis reactions

which lead to the P-C bond cleavage the temperatures required to effect the cleavage also lead to cluster breakdown with many Ru_2 clusters being formed.^[75-77] Exceptions include clusters (4) (see Figure 3.20) which are the only products, of the many isolated, which retain the Ru_3 core when $\text{Ru}_3(\text{CO})_9\text{L}_3$ ($\text{L} = \text{PPh}_3$, $\text{P}(3\text{-MeC}_6\text{H}_4)_3$ or $\text{P}(4\text{-MeC}_6\text{H}_4)_3$) clusters are pyrolysed.^[75] The relatively mild conditions employed in the formation of (2) result in retention of the Ru_3 core in all but two of the products, one of which appears to be a Ru_4 species, and the other a monoruthenium complex. Conversely the majority of products isolated from the pyrolysis of phosphane-substituted tri-osmium clusters, in which oxidative addition across a P-C bond is observed, retain the Os_3 triangle, reflecting the higher stability of the Os_3 core.^[78] Indeed one of these products is the osmium analogue of (4). The $\mu\text{-PPh}_2$ groups in the tri-iron cluster $\text{Fe}_3(\text{CO})_8(\mu\text{-H})_2(\mu\text{-PPh}_2)_2$ are obtained from P-H bond cleavage^[79] not P-C bond cleavage as found for the Ru and Os clusters. P-Ph bond cleavage with retention of the aryl-group in the cluster by a M-C σ -bond has also been observed for iridium complexes.^[80]

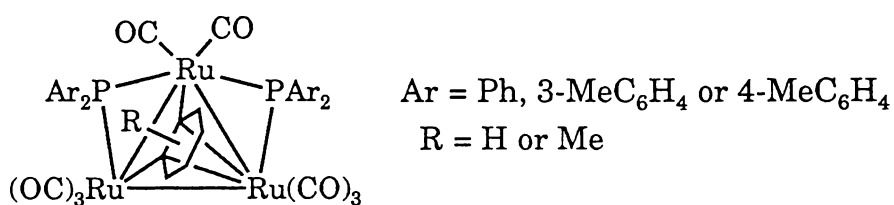
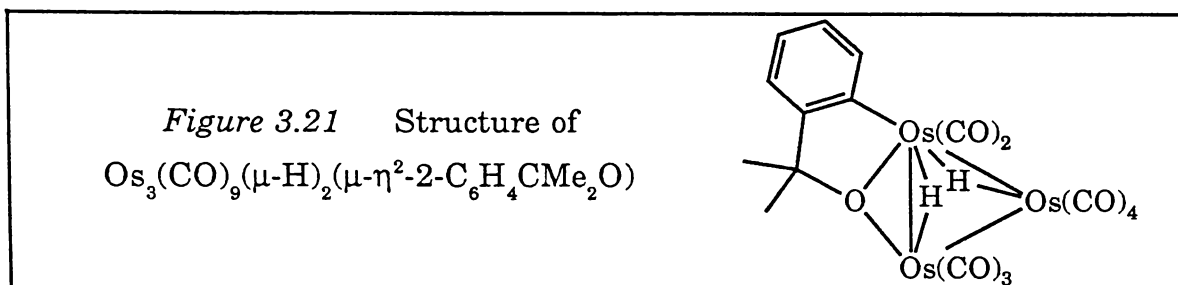


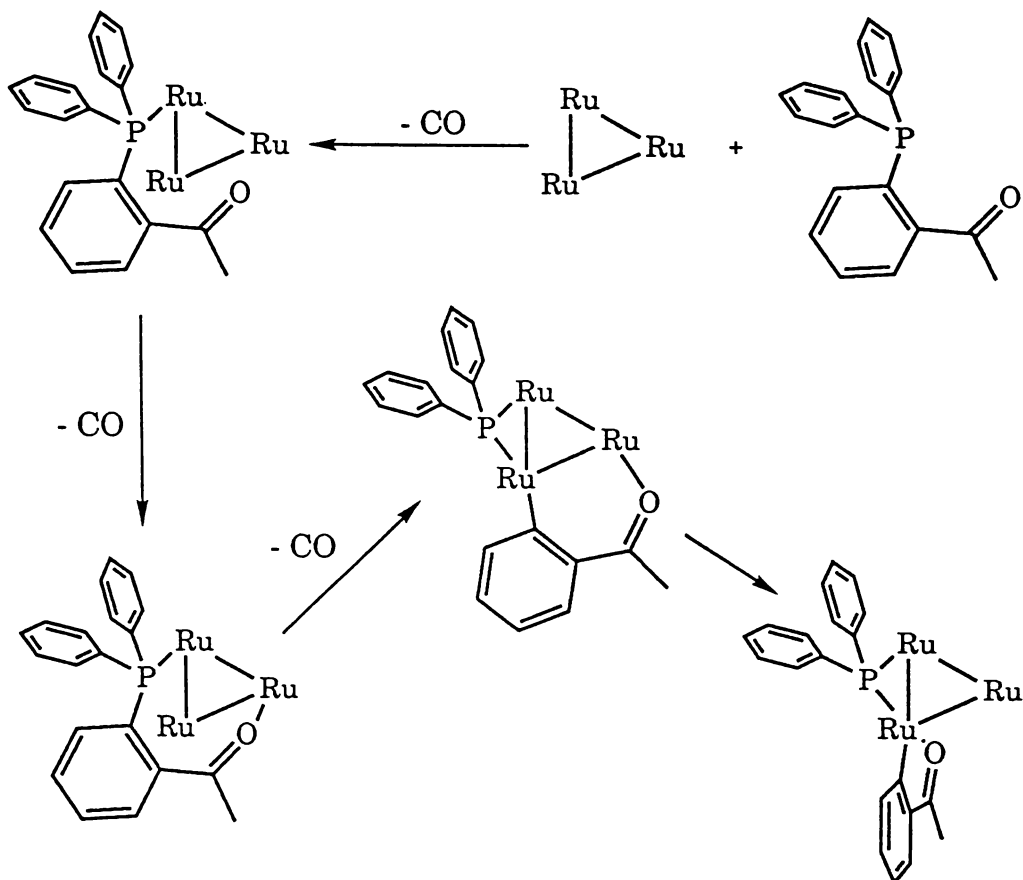
Figure 3.20 Structure of $\text{Ru}_3(\text{CO})_8(\mu\text{-PAr}_2)_2(\mu_3\text{-}\eta^2\text{-C}_6\text{H}_4\text{R})$ (4).

(2) is the first poly-nuclear iron-group compound incorporating a *cyclo*-metallated acetophenone ligand. The one other iron-group complex which incorporates this ligand is the mono-nuclear Ru complex, $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\eta^2\text{-2-C}_6\text{H}_4\text{COMe})$ (5) which is prepared from the direct reaction of acetophenone with the trigonal bi-pyramidal complex $\text{Ru}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\eta^2\text{-OOCMe})$ (6).^[70] The closest osmium analogue of (2) is

$\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\mu\text{-}\eta^2\text{-2-C}_6\text{H}_4\text{CMe}_2\text{O})$ (see Figure 3.21) in which the oxygen atom bridges one of the Os-Os bonds. This cluster, which was obtained stepwise by refluxing $\text{Os}_3(\text{CO})_{12}$ and 1-methyl-1-phenylethanol first in xylene and then in n-nonane,^[81] has a single C-O bond and an extra methyl group occupies the released site on the carbon atom.



The planar geometry found for the $\text{C}_6\text{H}_4\text{C(OMe)}$ moiety in (2) is in accord with other *ortho*-metallated α,β -unsaturated compounds studied by X-ray crystallography. However, beyond this, the remarkably constant geometry found in a wide range of other *ortho*-metallated aromatic ketones^[60,61,82] is not found for the two ruthenium complexes (2) and (5). In the other complexes the C-O-M-C-C ring is essentially planar with the C=O bond slightly longer than expected for a true double bond, while the $\text{C}(sp^2)\text{-C}(sp^2)$, M-C and M-O single bonds are short. These features are consistent with delocalised π -bonding over the whole ring. In both of the nearly planar ruthenium complexes the Ru-C and Ru-O bond lengths are normal for single bonds, suggesting no delocalised π -bonding involving the Ru centre. The bond distances around the rest of the C-O-Ru-C-C ring in (2) and (5) differ. For (5) these distances are similar to the other *ortho*-metallated complexes, suggesting delocalised π -bonding over the entire acetophenone ligand. In cluster (2) the C=O bond and the $\text{C}(sp^2)\text{-C}(sp^2)$ bond distances are essentially the same as the comparable bond distances in free acetophenone,^[67] suggesting little, or no, delocalised π -bonding within the entire C-O-Ru-C-C ring.



Scheme 3.3

The formation of (2) from (3) probably goes via two intermediates. In the first the phosphane ligand remains intact bridging the Ru(1)-Ru(2) bond (see Scheme 3.3 in which the carbonyl ligands have been omitted for simplicity) followed by attack at the phosphorus-carbon bond by Ru(2) to give bridging PPh₂ and $\overline{\text{C}_6\text{H}_4\text{COMe}}$ moieties. The $\mu\text{-}\eta^2\text{-C}_6\text{H}_4\text{COMe}$ ligand then rearranges to give (2). A similar pathway to P-C bond cleavage is postulated for the formation of $\text{Ru}_3(\text{CO})_9[\mu\text{-}\eta^2\text{-C(O)Ph}][\mu_3\text{-}\eta^2\text{-PPh(C}_5\text{H}_4\text{N)}]$ from the monosubstituted cluster $\text{Ru}_3(\text{CO})_{11}[\text{PPh}_2(\text{C}_5\text{H}_4\text{N})]$ under mild conditions.^[83] Osmium clusters analogous to the ruthenium ones in Scheme 3.3 were isolated from the pyrolysis of PPh₃-substituted $\text{Os}_3(\text{CO})_{12}$ discussed earlier.

The P-C bond cleavage observed for the β -ketophosphane prepared in this work is not observed when the α,β -unsaturated group is a C=C double bond. This is illustrated by the pyrolysis reactions of $\text{Ru}_3(\text{CO})_{10}(\text{sp})$

and its derivatives, in which the products retain the P-C bond to the α,β -unsaturated group.^[33,34-84]

In conclusion, this work has presented a viable route to the β -ketophosphane ligand (2-acetylphenyl)diphenylphosphane and justified the interest in this ligand, as illustrated by its chemistry on $\text{Ru}_3(\text{CO})_{12}$. The major product isolated has shown the comparison with the sp ligand to be superficial and that the differences in reactivities are marked. The ease with which (2-acetylphenyl)diphenylphosphane was transferred onto the Ru centre, as found for other phosphanes, has paved the way for subsequent work on this ligand with other metal systems.

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Chapter Four

CHAPTER FOUR

ATTEMPTED TRANSMETALLATION OF ORTHO-MANGANATED ARYL KETONES WITH Cu(II)

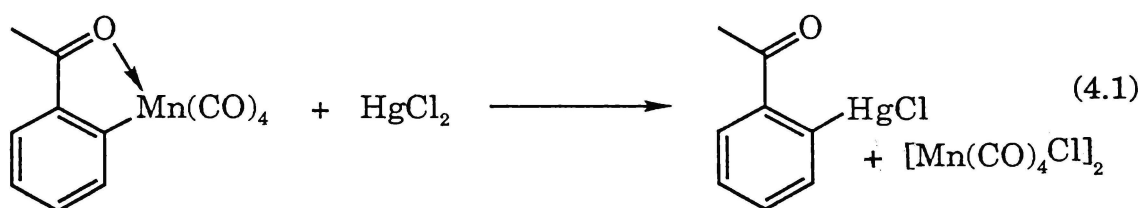
4.1 INTRODUCTION

Organo-copper reagents find wide application in organic synthesis as they enter into a wide range of specific reactions.^[1] Some of the more important reactions include the reaction of lithium organocopper reagents R_2CuLi with alkyl halides $R'X$ to give good yields of the cross-coupling products RR' ,^[2] with α,β -unsaturated aldehydes and ketones to give conjugate addition products in a reaction closely related to the Michael reaction^[3] or with themselves in the presence of O_2 to give symmetrical RR species.^[4] Organo-copper compounds are also thought to be intermediates in many copper catalysed reactions. These include the decarbonylation of aryl carboxylic acids with copper metal in the presence of quinoline^[5] and the Ullmann reaction which involves the coupling of aryl halides in the presence of copper metal.^[6]

Common routes to organo-copper species involve reaction of aryl-lithium reagents with copper(II) salts or the reaction of $R'Cu$ species with RLi to give $RR'CuLi$ reagents. However these methods do not have

unlimited application, especially when reactive functional groups are present on the organic fragment.

Similar problems are encountered in the preparation of RHgX species from RLi and HgX_2 and in direct mercuration reactions. The RLi routes cannot be used where there are functional groups on the arene that will react with RLi while direct mercuration is often not site-specific, giving a mixture of isomers or indeed the wrong isomer. Aryl ketones such as acetophenone and benzophenone provide a clear illustration of these problems. For example, in the case of acetophenone direct mercuration occurs at the methyl group rather than on the ring^[7] and the aryl-lithium route is precluded by the presence of the ketone function, while for benzophenone a mixture of isomers is generated by direct mercuration. Work done initially by Gommans^[8] and more fully by Cooney^[9] has shown the feasibility of site-specific mercuration of aryl ketones via transmetallation^[10] of the *ortho*-manganated derivatives as shown in Equation 4.1.



The Mn(CO)_4 group is readily displaced by HgCl_2 to give the corresponding *ortho*-aryl-mercury(II) chloride. Transmetallation is site specific, with no trace of other isomers and with good yields. The solvent of choice for these reactions is methanol as the products are generally insoluble and precipitate from the otherwise homogeneous solution, making the work-up straightforward. Transmetallation of aryl-mercury species has also been used in the preparation in a number of other organometallic compounds; to prepare aryl-gold species from gold(III) salts^[11-13] and organo-arsenic compounds from arsenic(III) halides.^[14-16]

If these specific transmetallation reactions used for the mercury system could be applied to the copper system then one should be able to make site specific keto arene cuprates. The resulting cuprates would be of wide use in organic synthesis.

4.2 OXIDATION OF ORTHO-MANGANATED ARYL KETONES WITH Cu(II) IN METHANOL

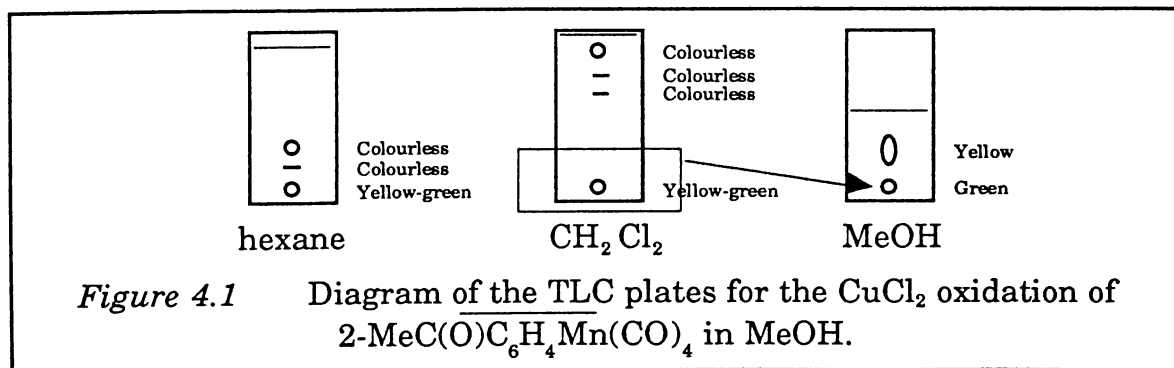
The structures of compounds (1) to (6) discussed in the following sections are shown in Scheme 4.6 and Scheme 4.7.

4.2.1 Experimental

All reactions were performed with the exclusion of oxygen and water using solvents dried by standard methods as discussed in Chapter One. Anhydrous CuCl_2 was prepared as described in Section 1.3.2. Oxidation was generally achieved by refluxing the *ortho*-manganated aryl ketone with a 1 to 10-fold excess of CuCl_2 in an alcoholic solvent.

4.2.2 CuCl_2 Oxidation of η^2 -(2-acetylphenyl)tetracarbonyl-manganese in MeOH

A pale green solution of η^2 -(2-acetylphenyl)tetracarbonyl-manganese (**1a**) (0.286 g, 1.0 mmol) and CuCl_2 (0.134 g, 1.0 mmol) in MeOH (10 ml) was refluxed for 2 hours to give a dark green solution. A further 22 hours refluxing resulted in a yellow-brown solution with a brown precipitate which turned pale green on standing. TLC of the solution using three different solvents indicated the presence of four different colourless compounds and one yellow compound (see Figure 4.1).



PLC (silica gel) using 60-80°C petroleum spirits/dichloromethane (1:1) eluent gave four products: (i) acetophenone (**3a**), (0.009 g, 8 %) a colourless liquid identified by its GC mass spectrum, m/e 120 (M)⁺, m/e 105 ($M - Me$)⁺ and m/e 77 ($M - COMe$)⁺, ¹H nmr spectroscopy (CDCl₃) (δ 7.91 Ar-**H** *m*, 7.52 Ar-**H** *m* and 2.61 -CCH₃ *s*); (ii) 2'-chloroacetophenone (**2a**), (0.034 g, 22 %) a colourless liquid identified by its GC mass spectrum, m/e 154,156 (M)⁺, m/e 139,141 ($M - Me$)⁺, m/e 111,113 ($M - COMe$)⁺ and m/e 75 ($M - COMe - HCl$)⁺; (iii) 3-methoxy-3-methylphthalide (**5a[i]**), (0.028 g, 16 %) a colourless oil identified by its GC mass spectrum, m/e 163 ($M - Me$)⁺, m/e 147 ($M - OMe$)⁺, m/e 133 ($M - Me - CH_2O$)⁺, m/e 105 ($M - Me - CH_2O - CO$)⁺, m/e 104 ($M - OMe - COMe$)⁺, m/e 77 ($M - Me - CH_2O - 2(CO)$)⁺ and m/e 76 ($M - COOMe - COMe$)⁺ (see Section 4.2.2.1); and its ¹H nmr spectrum (CDCl₃) (δ 7.80 Ar-**H** *dt* 1H, 7.72 Ar-**H** *td* 1H, 7.59 Ar-**H** *td* 1H, 7.49 Ar-**H** *dt* 1H, 3.07 -OCH₃ *s* 3H and 1.83 -CCH₃ *s* 3H) (see Section 4.2.2.2) and ¹³C nmr spectroscopy (CDCl₃) (δ 168.1 -C_{Ar}C(O)O- *s*, 147.6 -C_{Ar}C_{Ar}(C_{Ar})C(O)- *s*, 134.6 Ar *d*, 130.6 Ar *d*, 127.4 -C_{Ar}C_{Ar}(C_{Ar})CO- *s*, 125.6 Ar *d*, 122.2 Ar *d*, 108.8 -C(OMe)(Me)O- *s*, 51.3 -OCH₃ *q* and 25.3 -CCH₃ *q*) (see Section 4.2.2.4); (iv) colourless methyl 2-acetylbenzoate (**4a[i]**), (0.022 g, 12 %) a colourless oil identified by its GC mass spectrum, m/e 163 ($M - Me$)⁺, m/e 147 ($M - OMe$)⁺, m/e 133 ($M - Me - CH_2O$)⁺, m/e 105 ($M - Me - CH_2O - CO$)⁺, m/e 104 ($M - OMe - COMe$)⁺, m/e 77 ($M - Me - CH_2O - 2(CO)$)⁺ and m/e 76 ($M - COOMe - COMe$)⁺ (see Section 4.2.2.1); ¹H nmr spectroscopy (CDCl₃) (δ 7.84 Ar-**H** *m* 1H, 7.53 Ar-**H** *m* 3H, 3.90 -C(O)OCH₃ *s* 3H and 2.54 -C(O)CH₃ *s* 3H) (see Section 4.2.2.3) and ¹³C nmr spectroscopy (CDCl₃) (δ 134.1 Ar *d*, 132.1 Ar *d*, 131.8 Ar *d*, 128.6 Ar *d*, 54.6 -C(O)OCH₃ *q* and 31.9 -C(O)CH₃ *q*) (see Section 4.2.2.5).

The reaction was repeated as above under one atmosphere pressure of CO with no discernible effect on product ratios or reaction rates.

4.2.2.1 Mass spectra of methyl 2-acetylbenzoate and 3-methoxy-3-methylphthalide

In the mass spectrum of the ester (**4a[i]**) three distinct breakdown pathways, as shown in Scheme 4.1, are observed: the first pathway consists of bond cleavages involving the C-C single bond next to C=O functionalities to give the series m/e 163, 147, 104 and 76. The second pathway also begins with loss of a methyl group to give the m/e 163 fragment. However, the two pathways diverge at this point with rearrangement of the 163 ion to give the relatively stable bicyclic species $\text{MeO}\overline{\text{CC}_6\text{H}_4\text{C(O)O}}^+$. This is followed by loss of formaldehyde to give the m/e 133 ion with subsequent loss of two CO groups. The third pathway is similar to the second in that a bicyclic species is also formed, but it begins with loss of a methoxy group to give a m/e 147 fragment, which rearranges to give the relatively stable bicyclic species $\text{Me}\overline{\text{CC}_6\text{H}_4\text{C(O)O}}^+$. This is followed by loss of COMe to give the m/e 104 ion with subsequent loss of CO.

The similarity of the mass spectrum of the phthalide (**5a[i]**) (see Figure 4.2) compared to that of the ester (**4a[i]**) can be rationalised by comparison of the structure of (**5a[i]**) with two of the breakdown fragments found for (**4a[i]**). The rearrangements that took place in pathways two and three (see Scheme 4.1) for (**4a[i]**) have occurred in compound (**5a[i]**) before the loss of the first fragment. Hence, the bicyclic m/e 163 and 147 fragments shown in Scheme 4.1 are readily formed by loss of either a methyl or methoxy group from the parent ion of (**5a[i]**) as shown in Scheme 4.2, with subsequent breakdown as for (**4a[i]**). The different base peaks for (**5a[i]**) of 147 and for (**4a[i]**) of 163 can be explained by the fact that one breakdown pathway found for (**4a[i]**) is not available for phthalide

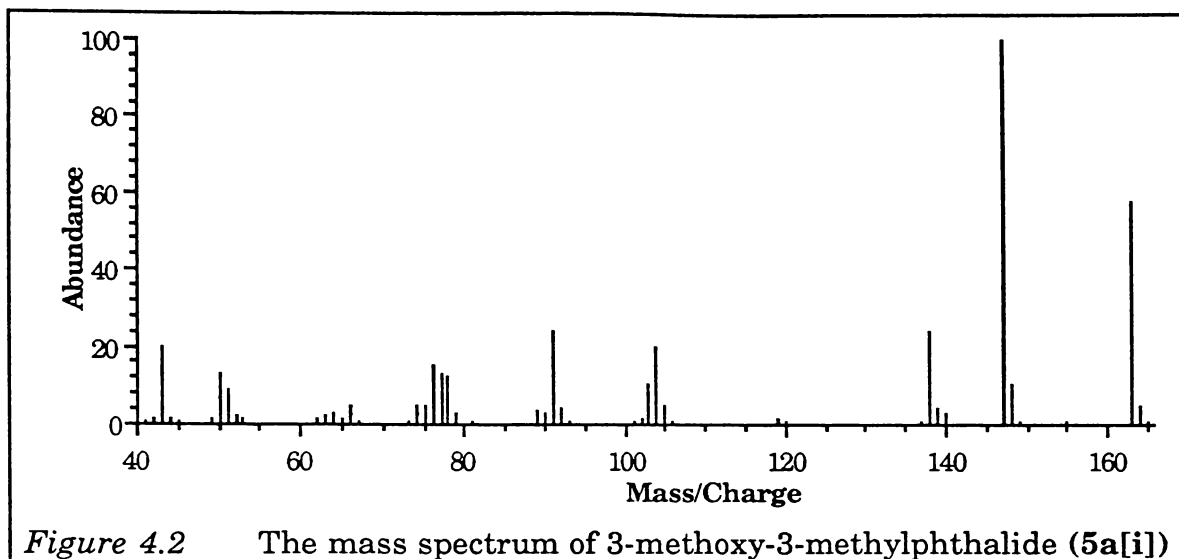
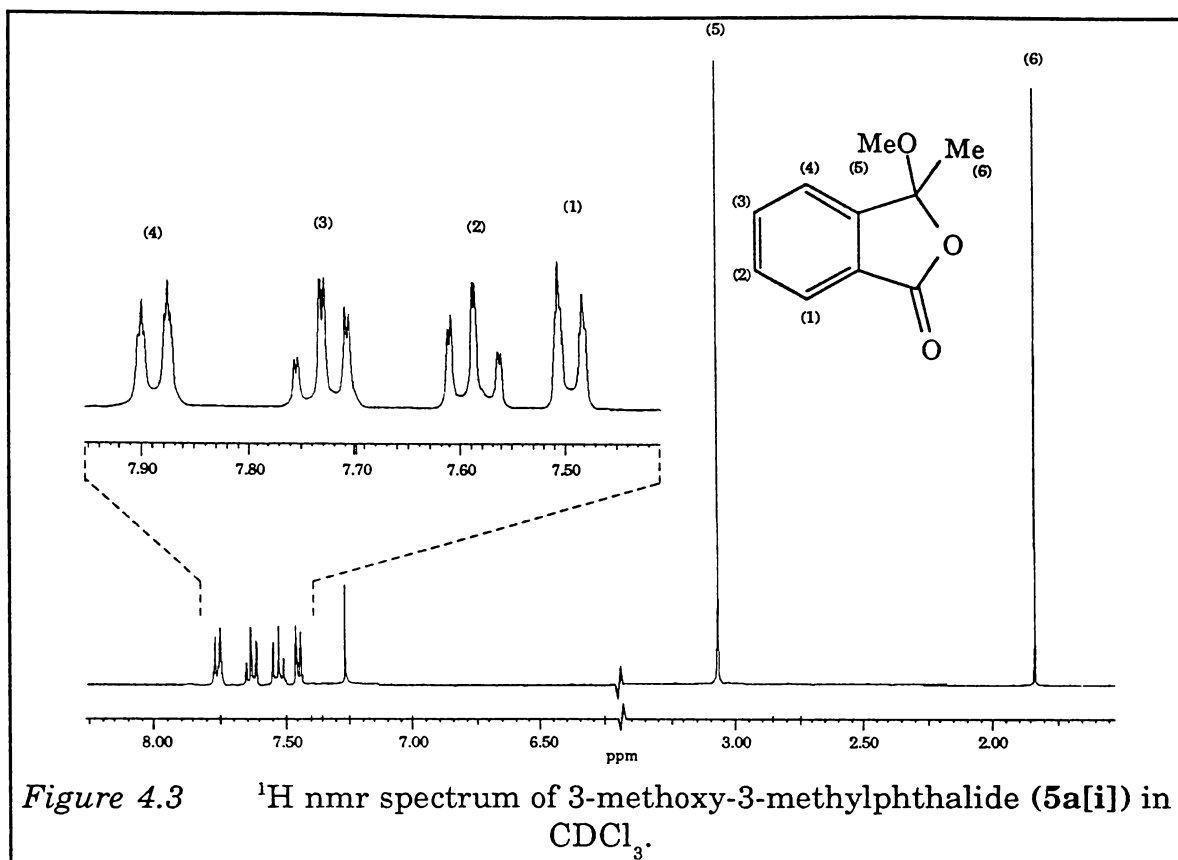


Figure 4.2 The mass spectrum of 3-methoxy-3-methylphthalide (5a[i])

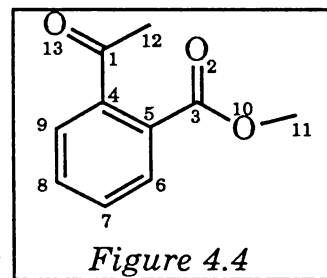
4.2.2.2 ^1H nmr spectrum of 3-methoxy-3-methylphthalide

The ^1H nmr spectrum of 3-methoxy-3-methylphthalide (5a[i]), as shown in Figure 4.3, recorded in CDCl_3 is in accordance with the unsymmetrically 1,2-substituted phenyl ring, together with the methoxy and the methyl functionalities of a methoxyphthalide derivative. H(1) a *ddd* appears as a *dt* (δ 7.80; $3J\text{-H}(2)$ 7.6 Hz, $4J\text{-H}(3)$ and $5J\text{-H}(4)$ 0.8 Hz) as the long range four and five bond couplings to H(3) and H(4) are unresolvable, as indeed are all the long range H-H couplings around this phenyl ring. In conjunction with the three-bond proton-proton couplings around the phenyl ring being unresolvable from the 7.6 Hz found for H(1) to H(2), this leads to a simpler spectrum than would be expected. H(2) a *ddd* appears as a *td* (δ 7.72; $3J\text{-H}(1)$ and $3J\text{-H}(3)$ 7.6 Hz, $4J\text{-H}(4)$ 0.8 Hz), H(3) a *ddd* appears as a *td* (δ 7.59; $3J\text{-H}(2)$ and $3J\text{-H}(4)$ 7.6 Hz, $4J\text{-H}(1)$ 0.8 Hz) and H(4) a *ddd* appears as a *dt* (δ 7.49; $3J\text{-H}(3)$ 7.6 Hz, $4J\text{-H}(2)$ and $5J\text{-H}(1)$ 0.8 Hz). H(5) a 3H singlet at δ 3.07 is consistent with a methoxy methyl group (compared to δ 3.00 for the same compound in $\text{CCl}_4^{[18]}$) and H(6) a 3H singlet at δ 1.83 (compared to δ 1.74 for the same compound in $\text{CCl}_4^{[18]}$) is normal for a methyl group bonded to a carbon atom which is in turn singly bonded to two oxygen atoms.



4.2.2.3 ^1H nmr spectrum of methyl 2-acetylbenzoate

The ^1H nmr spectrum of methyl 2-acetylbenzoate (4a[i]) was recorded in CDCl_3 . The resulting spectrum is consistent with the formulation of (4a[i]) as shown in Figure 4.4. The 3H singlet found at δ 2.54, as expected for the protons of



a methyl group attached to a carbonyl group, can be assigned to H(12) and assignment of the 3H singlet at δ 3.90 to H(11) is consistent with the protons of a methyl group attached to the oxygen atom of a carboxyl group. The signals from the aryl protons H(6), H(7), H(8) and H(9) are found in the two multiplets centred at δ 7.84 and 7.53. The corresponding resonances described in a previous report in CDCl_3 are δ 2.49 (s H(12)), 3.93 (s H(11)) and 7.43-8.15 (m H(6), H(7), H(8) and H(9)).^[19]

4.2.2.4 ^{13}C nmr spectrum of 3-methoxy-3-methylphthalide

The ^{13}C nmr spectrum of 3-methoxy-3-methylphthalide (**5a[i]**) in CDCl_3 , shown in Appendix Six, can be assigned as follows. The four doublet carbon atoms found on the aryl ring can be assigned to the four more intense signals in the δ 120 to 140 region (δ 134.6, 130.6, 125.6 and 122.2). The two quartets found at δ 51.3 and 25.3 can be assigned to the methoxy methyl carbon atom and to the methyl carbon atoms respectively. The singlet signals at δ 168.1, 127.4 and 147.6 are as would be expected for the carbon atom of a carboxyl group, an aryl carbon atom bonded to a sp^3 carbon and for an aryl carbon atom bonded to the sp^2 carbon atom of a carbonyl group respectively. The remaining singlet signal found at δ 108.8 is reasonable for a sp^3 carbon atom moved downfield by the presence of two directly bonded sp^3 oxygen atoms and one sp^2 aryl carbon atom.

4.2.2.5 ^{13}C nmr spectrum of methyl 2-acetylbenzoate

The ^{13}C nmr spectrum of methyl 2-acetylbenzoate (**4a[i]**) in CDCl_3 further substantiates its formulation as $2\text{-MeOC(O)C}_6\text{H}_4\text{C(O)Me}$, with signals at δ 31.9 (C(12)) and 54.6 (C(11)) for the methyl carbon atoms and at δ 128.6, 131.8, 132.2 and 134.1 (C(6), C(7), C(8) and C(9)) for the doublet aryl carbon atoms. The singlet carbon atoms C(1), C(3), C(4) and C(5) were not observed above the noise.

4.2.3 CuCl_2 Oxidation of η^2 -(2-benzoylphenyl)tetracarbonyl-manganese in MeOH

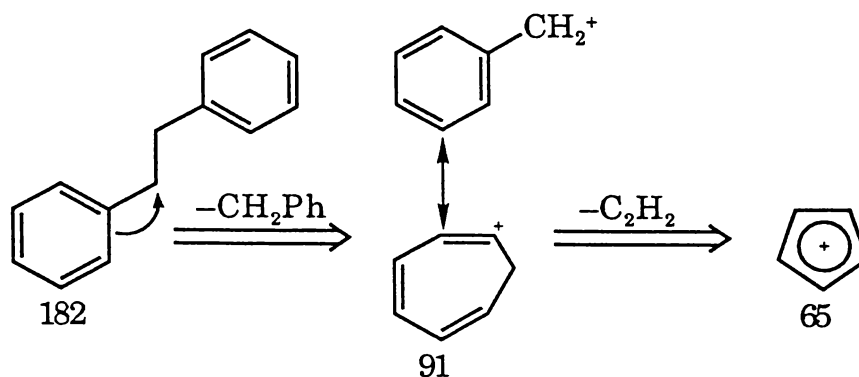
A solution of η^2 -(2-benzoylphenyl)tetracarbonylmanganese (**1b**) (0.341 g, 1.0 mmol) and CuCl_2 (0.134 g, 1.0 mmol) in MeOH (10 ml) was refluxed under N_2 for 48 hours to give a pale green solution. PLC (silica gel) using 40-60°C petroleum spirits/dichloromethane (7:3) eluent gave five bands: (i) $[\text{Mn}(\text{CO})_4\text{Cl}]_2$, (0.016 g, 8 %) a pale yellow solid identified by its infrared spectrum $\nu(\text{CO})_{\text{hexane}}$ (2084 w, 2046 s, 2015 s and 1984 m) cm^{-1} ;[20] (ii) tentatively identified as 1,2-diphenylethane, (0.015 g,

8 %) a white solid identified by its GC mass spectrum, m/e 182 (M)⁺; m/e 104 (M - PhH)⁺; m/e 91 (M - CH₂Ph)⁺ and m/e 65 (M - CH₂Ph-C₂H₂)⁺ (see Section 4.2.3.1); (iii) 2-chlorobenzophenone (**2b**), (0.061 g, 29 %) a colourless oil identified by its GC mass spectrum, m/e 216,218 (M)⁺; m/e 139,141 (M - Ph)⁺; m/e 111,113 (M - CPh)⁺; m/e 105 (M - C₆H₄Cl)⁺ and m/e 77 (M - COC₆H₄Cl)⁺ (see Section 4.2.3.1); (iv) benzophenone (**3b**), (0.048 g, 26 %) a colourless oil identified by its GC mass spectrum, m/e 182 (M)⁺; m/e 105 (M - Ph)⁺ and m/e 77 (M - CPh)⁺ (see Section 4.2.3.1); and (v) methyl 2-benzoylbenzoate (**4b[i]**), (0.058 g, 24 %) a colourless oil identified by its GC mass spectrum, m/e 240 (M)⁺; m/e 209 (M - OMe)⁺; m/e 163 (M - Ph)⁺; m/e 105 (M - C₆H₄COOMe)⁺ and m/e 77 (M - COC₆H₄COOMe)⁺ (see Section 4.2.3.2).

A mechanism as to the formation of 1,2-diphenylethane from the reaction of (**1b**) with CuCl₂ in MeOH is unclear. At first glance its mass spectrum is very similar to that of benzophenone, with the one major exception, the m/e 91 peak (which would correspond to breaking of the CH₂-CH₂ bond) found for 1,2-diphenylethane and not for benzophenone. It should also be noted that benzophenone had a different R_f than found for 1,2-diphenylethane.

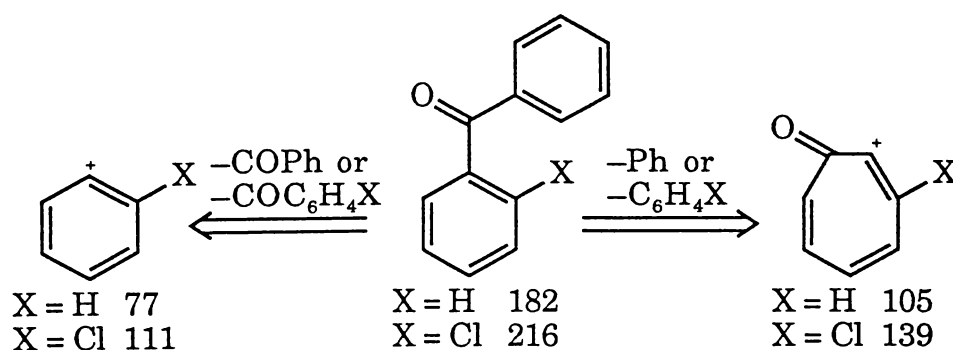
4.2.3.1 Mass spectra of 1,2-diphenylethane, 2-chlorobenzophenone and benzophenone

The mass spectra of 1,2-diphenylethane (PhCH₂CH₂Ph), 2-chlorobenzophenone (**2b**) and benzophenone (**3b**) all gave library matches of greater than 90 %. The spectrum of what was tentatively assigned as PhCH₂CH₂Ph is simple with only three major peaks: the molecular ion of m/e 182, half the molecular ion formed by breaking of the CH₂-CH₂ bond to give m/e 91, and the m/e 65 peak corresponding to loss of ethylene from the 91 peak as shown in Scheme 4.3. One minor peak at m/e 104 is a result of the loss of benzene from the molecular ion.



Scheme 4.3

The mass spectra of (2b) and (3b), not too surprisingly considering they differ only by a chlorine atom on one of the phenyl rings, are based on the same breakdown pathways, with mass differences appearing when the charged fragment from (2b) retains the chlorine atom. The spectra are dominated by peaks arising from bond cleavage on either side of the carbonyl group. Hence, due to the symmetry of (3b) only the molecular ion (m/e 182) and two fragments related to $X = H$ (m/e 105 and m/e 77) are observed (see Scheme 4.4). For compound (2b) the equivalent three ions corresponding to $X = Cl$ (m/e 216, m/e 139, m/e 111) along with the two fragment ions with $X = H$ (m/e 105, m/e 77) and a weak m/e 181 ($M - Cl$)⁺ fragment ion are observed.



Scheme 4.4

4.2.3.2 Mass spectrum of methyl 2-benzoylbenzoate

Most of the envelopes found in the mass spectrum of methyl 2-benzoylbenzoate (4b[i]) can be explained in terms of Scheme 4.4 using $X = C(O)OMe$. Using this analogy one would predict envelopes for the

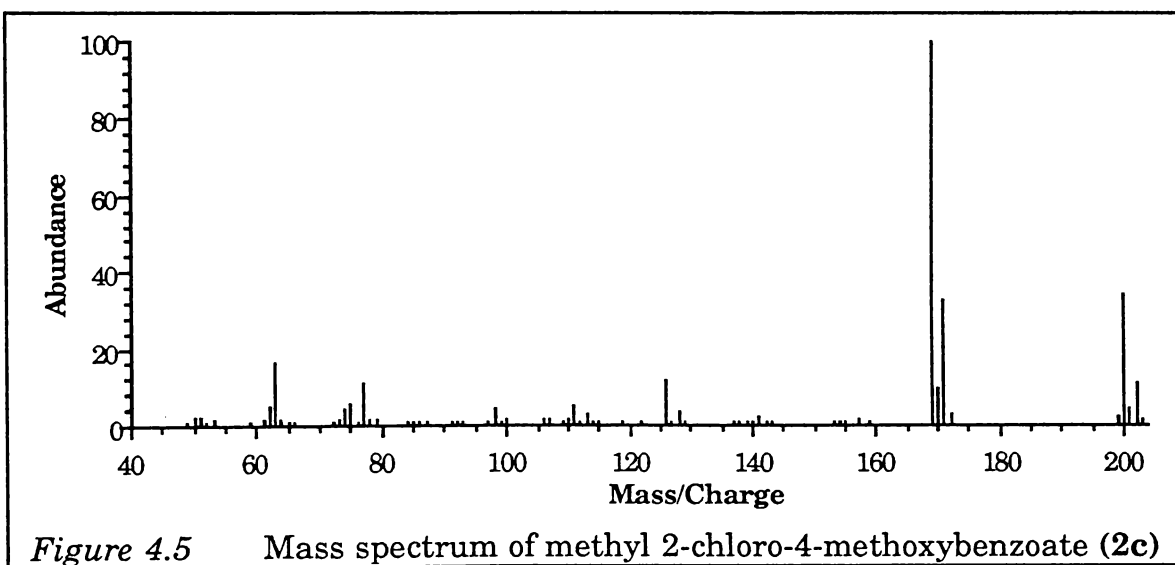
X = C(O)OMe series at m/e values of 240, 163, and 135 and for the X = H series at 105 and 77. All these envelopes are observed except for the m/e 135 ion which would result from the loss of PhCO from the parent ion. The absence of the 135 envelope coupled with the fact that the 163 fragment is the dominant ion suggest that rearrangement of the 163 (M -Ph) fragment, as found for the acetyl analogue (**4a[i]**) and shown in Scheme 4.1, to the stable bicyclic ion $2\text{-MeOC}\overset{\text{C}}{\text{C}}_6\text{H}_4\text{-C(O)O}^+$ occurs. Two additional envelopes are also observed: the first, at m/e 181 corresponds to the M -X peak also observed for (**2a**) and second at m/e 209 is consistent with loss of OMe of the methyl ester function.

4.2.4 CuCl₂ Oxidation of η^2 -(2-carbomethoxy-5-methoxy-phenyl)tetracarbonylmanganese in MeOH

A solution of η^2 -(2-carbomethoxy-5-methoxyphenyl)tetracarbonylmanganese (**1c**) (0.038 g, 0.12 mmol) and CuCl₂ (0.016 g, 0.12 mmol) in MeOH (5 ml) was refluxed under N₂ for 24 hours. PLC (silica gel) of the resulting mixture using 40-60°C petroleum spirits/dichloromethane (1:1) eluent gave five bands of which only two were in sufficient quantities to characterise: (i) methyl 2-chloro-4-methoxybenzoate (**2c**), (0.009 g, 38 %) a colourless oil identified by its GC mass spectrum, m/e 200,202 (M)⁺; m/e 169,171 (M - OMe)⁺; m/e 141,143 (M - COOMe)⁺ (see Section 4.2.4.1); and (ii) dimethyl 4-methoxyphthalate (**4c[i]**), (0.009 g, 33 %) a colourless oil identified by its GC mass spectrum, m/e 224 (M)⁺; m/e 193 (M - OMe)⁺; m/e 165 (M - COOMe)⁺ and m/e 106 (M - 2(COOMe))⁺ (see Section 4.2.4.1); ¹H nmr spectroscopy (CDCl₃) (δ 7.82 Ar-H *d* 1H, 7.08 Ar-H *d* 1H, 7.00 Ar-H *dd* 1H, 3.93 -OCH₃ *s* 3H, 3.88 -C(O)OCH₃ *s* 3H and 3.88 -C(O)OCH₃ *s* 3H) (see Section 4.2.4.2) and ¹³C nmr spectroscopy (CDCl₃) (δ 168.9 -C(O)OMe *s*, 166.8 -C(O)OMe *s*, 162.1 ArOMe *s*, 135.7 ArC(O)O *s*, 131.6 Ar *d*, 122.2 ArC(O)O *s*, 115.8 Ar *d*, 113.5 Ar *d*, 55.7 -OCH₃ *q*, 52.7 -C(O)OCH₃ *q* and 52.5 -C(O)OCH₃ *q*) (see Section 4.2.4.2).

4.2.4.1 Mass spectra of methyl 2-chloro-4-methoxybenzoate and dimethyl 4-methoxyphthalate

The mass spectra of methyl 2-chloro-4-methoxybenzoate (**2c**) (see Figure 4.5) and dimethyl 4-methoxyphthalate (**4c[i]**) once again are based on cleavage of bonds adjacent to carbonyl functions. The spectrum for (**2c**) has only three major bands: these being the molecular ion m/e 200-202, m/e 169-171 resulting from cleavage of the carbonyl carbon methoxy bond and m/e 141,143 from the cleavage of the carbonyl carbon to aryl bond with loss of COOMe. For (**4c[i]**) the three envelopes observed at m/e 224, 193 and 165 are analogous to the three envelopes seen for (**2c**). The additional fragment observed at m/e 106 results from loss of the second COOMe group via cleavage of another carbonyl carbon aryl bond.

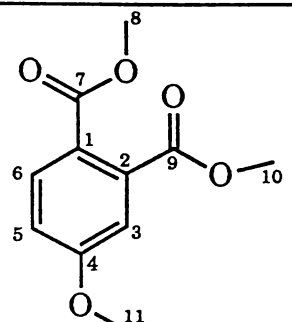


4.2.4.2 ^1H and ^{13}C nmr spectra of dimethyl 4-methoxyphthalate

The ^1H nmr spectrum of (**4c[i]**) is summarised in Table 4.1. It is consistent with both 1,2,4-trisubstitution of a benzene ring and the presence of two methyl ester groups and one methoxy group.

The ^{13}C nmr spectrum of (**4c[i]**) is also consistent with the formulation of dimethyl 4-methoxyphthalate. Peaks at δ 168.9 and 166.8 can be assigned to the two singlet ester carbon atoms C(7) and C(9), while

Table 4.1 ¹ H Nmr Spectrum for dimethyl 4-methoxyphthalate					
δ (ppm)	Multiplicities		J (Hz)	Assignment	
	3J	4J			
7.82	1H	d	-	8.7	6
7.08	1H	-	d	2.6	2
7.00	1H	d	d	8.7, 2.6	5
3.93	3H	s	-	-	11
3.88	3H	s	-	-	8 or 10
3.88	3H	s	-	-	10 or 8



the singlet at 162.1 arises from the aryl carbon, C(4), bonded to the methoxy group. The two remaining singlet carbon signals at 135.7 and 122.2 can be assigned to the aryl carbon atoms, C(2) and C(1) (probably the 122.2 signal due to the large upfield shift associated with an aryl carbon *para* to a methoxy group), which are bonded to the ester groups. The remaining three aryl carbon signals found at δ 131.6, 115.8 and 113.5 can be attributed to the three doublet carbon atoms, C(3), C(5) and C(6). The three quartets at δ 55.7, 52.7 and 52.5 are from the methoxy carbon atoms. Comparison of calculated and observed chemical shifts of the aryl carbon atoms are shown in Table 4.2.

Table 4.2 ¹³ C Nmr chemical shifts calculated for dimethyl 4-methoxyphthalate (4c[i])						
Group	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
δ_{benzene}	128.5	128.5	128.5	128.5	128.5	128.5
Z_{COOMe}	2.0(z1)	1.2(z0)	-0.1(zm)	4.3(zp)	-0.1(zm)	1.2(z0)
Z_{COOMe}	1.2(z0)	2.0(z1)	1.2(z0)	-0.1(zm)	4.3(zp)	-0.1(zm)
Z_{OMe}	-7.7(zp)	1.0(zm)	-14.4(z0)	31.4(z1)	-14.4(z0)	1.0(zm)
Calc.	124.0	132.7	115.2	164.1	118.3	130.6
Observed	122.2	135.7	113.5	162.1	115.8	131.6

4.3 OXIDATION OF ORTHO-MANGANATED ARYL KETONES WITH Cu(II) IN ETHANOL

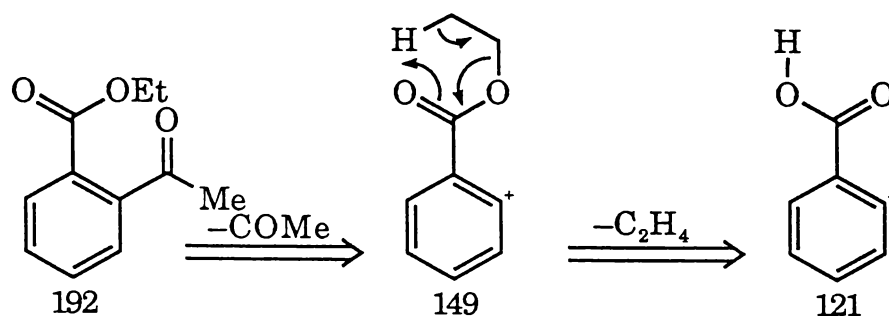
4.3.1 CuCl₂ Oxidation of η^2 -(2-acetylphenyl)tetracarbonyl-manganese in EtOH

A solution of (1a) (0.286 g, 1.0 mmol) and CuCl₂ (0.134 g, 1.0 mmol) in EtOH (10 ml) was refluxed for 24 hours to give a dark green solution. PLC (silica gel) using 60-80°C petroleum spirits/dichloromethane (1:1) eluent gave three bands: (i) acetophenone (3a), (0.010 g, 9%) a colourless liquid identified by its GC mass spectrum, m/e 120 (M)⁺; m/e 105 ($M - Me$)⁺ and m/e 77 ($M - COMe$)⁺; (ii) 2'-chloroacetophenone (2a), (0.028 g, 18%) a colourless liquid identified by its GC mass spectrum, m/e 154,156 (M)⁺; m/e 139,141 ($M - Me$)⁺; m/e 111,113 ($M - COMe$)⁺ and m/e 75 ($M - COMe-HCl$)⁺; (iii) a colourless oil of 1:2 mixture of 3-ethoxy-3-methylphthalide, $\overline{C_6H_4C(O)OC(Me)OEt}$ (5a[ii]), (0.020 g, 10%) identified by its GC mass spectrum, m/e 177 ($M - Me$)⁺; m/e 147 ($M - OEt$)⁺ and ($M - Me-CH_2O$)⁺; m/e 119 ($M - Me-CH_2O-CO$)⁺; m/e 104 ($M - OEt-COMe$)⁺; m/e 91 ($M - Me-CH_2O-2(CO)$)⁺ and m/e 76 ($M - COOEt-COMe$)⁺ (see Section 4.3.1.1); and ethyl 2-acetylbenzoate (4a[ii]), (0.010 g, 10%) identified by its GC mass spectrum, m/e 177 ($M - Me$)⁺; m/e 149 ($M - COMe$)⁺; m/e 147 ($M - OEt$)⁺; m/e 121 ($M - COMe-C_2H_4$)⁺; m/e 105 ($M - Me-MeCHO-CO$)⁺; m/e 104 ($M - OEt-COMe$)⁺; m/e 91 ($M - Me-CH_2O-2(CO)$)⁺ and m/e 76 ($M - COOEt-COMe$)⁺ (see Section 4.3.1.1).

4.3.1.1 Mass spectra of ethyl 2-acetylbenzoate and 3-ethoxy-3-methylphthalide

The mass spectra of ethyl 2-acetylbenzoate (4a[ii]) and 3-ethoxy-3-methylphthalide (5a[ii]) can be explained, with the exception of the m/e 121 peak found for (4a[ii]), in terms of the breakdown pathways for methyl analogues (4a[i]) and (5a[i]) shown in Schemes 4.1 and 4.2 and discussed in Section 4.2.2.1. Adjustments need only be made to allow for the change

of the -OMe group to an -OEt group. The m/e 121 peak is formed by loss of C_2H_4 from the m/e 149 ($M - COMe$)⁺ fragment (see Scheme 4.5)



Scheme 4.5

4.3.2 $CuCl_2$ Oxidation of η^2 -(2-benzoylphenyl)tetracarbonyl-manganese in EtOH

A solution of η^2 -(2-benzoylphenyl)tetracarbonylmanganese (**1b**) (0.348 g, 1.0 mmol) and $CuCl_2$ (1.34 g, 10 mmol) in EtOH (10 ml) was refluxed for 4 days. The solvent was then removed on a rotary evaporator and the residue extracted with dichloromethane (3 x 20 ml). The combined extracts were washed through an alumina column (2.5 x 5 cm, activity IV) with dichloromethane and the solvent volume reduced. PLC (silica gel) of the resulting solution using 60-80°C petroleum spirits/dichloromethane (1:1) eluent gave two isolable bands: (i) a colourless oil of a 1:2 mixture of benzophenone (**3b**), (0.029 g, 17 %) identified by its GC mass spectrum, m/e 182 (M)⁺, m/e 105 ($M - Ph$)⁺ and m/e 77 ($M - C(=O)Ph$)⁺ (see Section 4.2.3.1); and 2-chlorobenzophenone (**2b**), (0.061 g, 29 %) identified by its GC mass spectrum, m/e 216,218 (M)⁺, m/e 139,141 ($M - Ph$)⁺, m/e 111,113 ($M - C(=O)Ph$)⁺, m/e 105 ($M - C_6H_4Cl$)⁺ and m/e 77 ($M - COC_6H_4Cl$)⁺ (see Section 4.2.3.1); and (ii) ethyl 2-benzoylbenzoate (**4b[ii]**), (0.077 g, 36 %) a colourless oil identified by its GC mass spectrum, m/e 254 (M)⁺, m/e 209 ($M - OEt$)⁺, m/e 177 ($M - Ph$)⁺, m/e 149 ($M - C(=O)Ph$)⁺, m/e 105 ($M - C_6H_4COOEt$)⁺ and m/e 77 ($M - COC_6H_4COOEt$)⁺ (see Section 4.3.2.1); 1H nmr spectroscopy ($CDCl_3$) (δ 8.05 Ar-H *dd* 1H, 7.75 Ar-H *dd* 2H, 7.64-7.51 Ar-H *m* 3H, 7.44-7.37 Ar-H *m* 3H, 4.06

-OCH₂CH₃ *q* 2H and 1.05 -OCH₂CH₃ *t* 3H) (see Section 4.3.2.2) and ¹³C nmr spectroscopy (CDCl₃) (δ 196.9 -C(O)- *s*, 165.8 -C(O)OMe *s*, 141.7 ArC(O) *s*, 137.4 ArC(O) *s*, 133.3 Ar *d*, 132.5 Ar *d*, 130.2 Ar *d*, 129.8 Ar *d*, 129.7 Ar *d* 2C, 128.6 Ar *d* 2C, 127.8 Ar *d*, 51.6 -OCH₂CH₃ and 13.8 -OCH₂CH₃ *q*) (see Section 4.3.2.2).

4.3.2.1 Mass spectrum of ethyl 2-benzoylbenzoate

As for the methyl analogue (4b[i]) most of the envelopes found in the mass spectrum of ethyl 2-benzoylbenzoate (4b[ii]) can be explained in terms of Scheme 4.4, with X = C(O)OEt instead of X = C(O)OMe. The predicted envelopes for the X = C(O)OEt series would occur at *m/e* values of 254, 177, and 149 and for the X = H series at 105 and 77. All of these envelopes are observed along with an additional envelope at *m/e* 209, which is consistent with loss of OEt from the ethyl ester function.

The existence of the *m/e* 149 envelope suggests that substitution of the methyl ester found in (4b[i]) with the ethyl ester of (4b[ii]) destabilises the bicyclic rearrangement fragment ion such that some of the 177 fragment is able to lose CO.

4.3.2.2 ¹H and ¹³C nmr spectra of ethyl 2-benzoylbenzoate

Both the ¹H and ¹³C nmr spectra of (4b[ii]), recorded in CDCl₃, are consistent with the formulation of (4b[ii]) as 2-PhC(O)C₆H₄C(O)OEt with the one proviso that one of the singlet aryl carbon signals is hidden amongst the nine doublet aryl carbon signals which are found at δ 133.3, 132.5, 130.2, 129.8, 129.7 2C, 128.6 2C and 127.8. The two remaining aryl carbon signals are singlets located at δ 141.7 and 137.4. The carbonyl carbon resonance is normal at δ 196.9, as is the carboxyl carbon resonance at 165.8. The last two resonances at δ 51.6 *t* and 13.8 *q* are within normal ranges for the methylene and methyl carbons of an ethoxy group respectively.

In the ^1H nmr spectrum the signals for the ethoxy group are found at δ 4.06 *q* 2H, and 1.05 *t* 3H, compared with the δ 3.17 and 1.11 signals found for 1,3-dihydro-1-ethoxy-1-phenylisobenzofuran.^[21] The nine aryl protons occur in four envelopes: two *dd* at δ 8.05 1H and 7.75 2H, and two 3H multiplets at δ 7.64-7.51 and 7.44-7.37.

4.4 OXIDATION OF η^2 -(2-ACETYLPHENYL)TETRACARBONYLMANGANESE WITH Cu(II) IN THE PRESENCE OF PHENOL

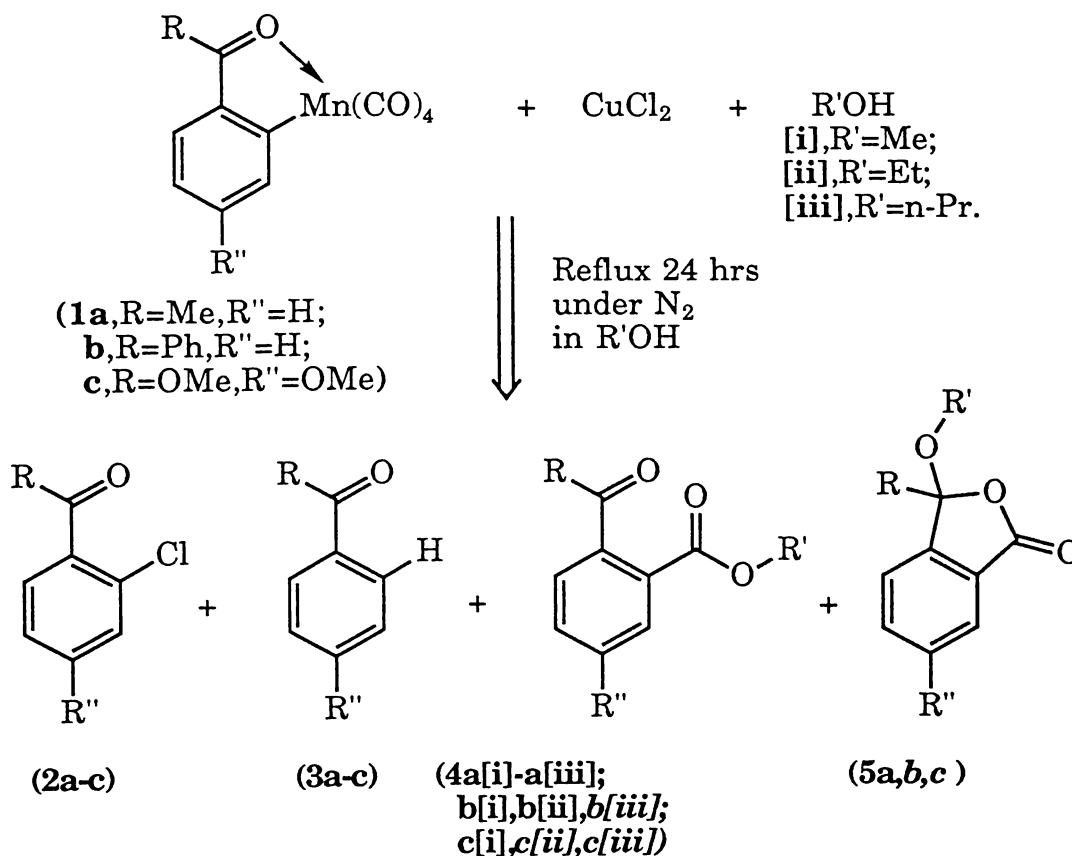
A solution of (1a) (0.286 g, 1.0 mmol), phenol (0.470 g, 5.0 mmol) and CuCl_2 (0.17 g, 1.2 mmol) in THF (10 ml) was refluxed for 92 hours. The cold reaction mixture was filtered and washed with THF (5 x 10 ml). The THF was removed on a rotary evaporator and the residue extracted with dichloromethane (5 x 10 ml). The combined extracts were filtered

Table 4.3 Mass spectral data for the products from the Cu(II) oxidation of (1a) in the presence of PhOH.				
Compound	<i>m/e</i> Fragment			
(3b)	120 M	105 <i>M</i> - Me	77 <i>M</i> - COMe	
(2b)	154 M	139 <i>M</i> - Me	111 <i>M</i> - COMe	
		75 <i>M</i> - COMe-HCl		
1H-Indene-1,3(2H)-dione (6) [§]	146 M	118 <i>M</i> - CO	104 <i>M</i> - C(O)CH ₂	
	90 <i>M</i> - 2(CO)	76 <i>M</i> - CH ₂ (CO) ₂		
Unknown	153	133	105	77
1-hydroxy-1-methyl-phthalide ^[22]	163 <i>M</i> - H	149 <i>M</i> - Me		
	147 <i>M</i> - OH	133 <i>M</i> - OMe		
	91 <i>M</i> - H-CO ₂ -CO	76 <i>M</i> - CH ₄ -CO ₂ -CO		
1,1'-oxybis[4-chlorobutane] ^ø	91 <i>M</i> - OCH ₂ CH ₂ CH ₂ CH ₂ Cl			
	55 <i>M</i> - OCH ₂ CH ₂ CH ₂ CH ₂ Cl-HCl			
Unknown	177	149	147	104 91
PhCH ₂ CH ₂ Ph [§]	182 M	91 <i>M</i> - CH ₂ Ph		
(5a[iv])	240 M	147 <i>M</i> - OPh	104 <i>M</i> - OPh-C(O)Me	
	91 <i>M</i> - C(O)OPh-CO			
(4a[iv])	240 M	147 <i>M</i> - OPh	104 <i>M</i> - OPh-C(O)Me	
	91 <i>M</i> - C(O)OPh-CO			
§ better than 90 % library match				
ø probably formed by chlorination of THF with ring opening				

and the solvent volume reduced to ~4 ml. PLC (silica gel) of the resulting solution using 40-60°C petroleum spirits/dichloromethane (1:1) eluent gave several colourless bands with $R_f > 0.75$ dispersed within the broad phenol band. These top bands were combined and analysed using GCMS (see Table 4.3); yields were not calculated.

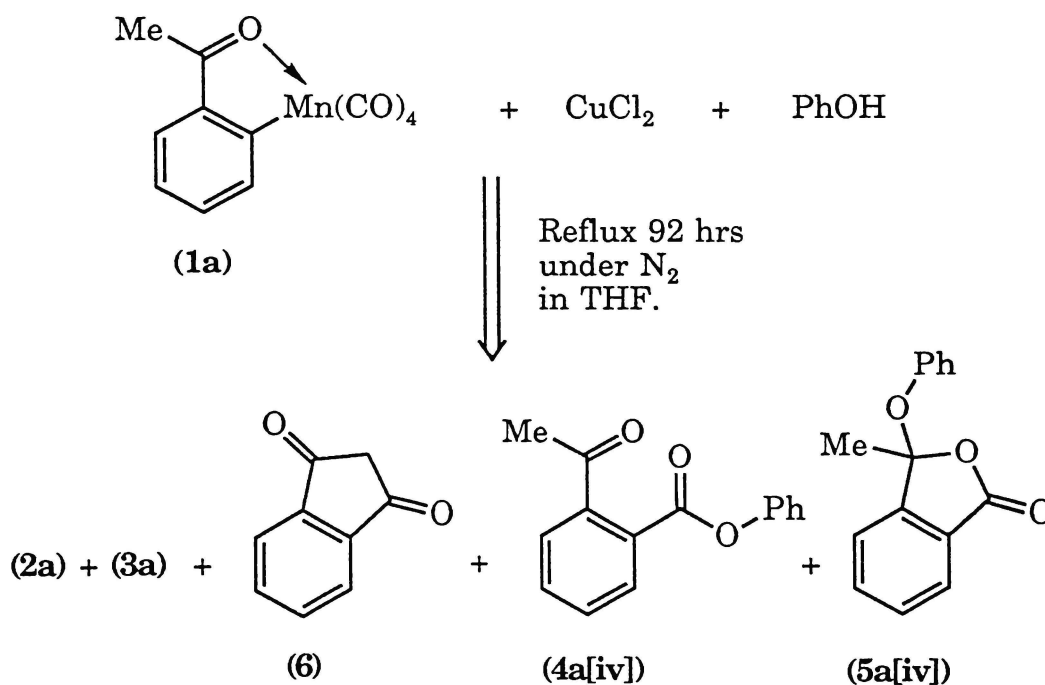
4.5 DISCUSSION

From the products it appears that the Cu^{2+} is acting as an oxidising agent rather than a transmetallating species. The major products isolated from the reactions of *o*-manganated aryl ketones with CuCl_2 in alcoholic solvents are summarised in Scheme 4.6 and Scheme 4.7. Aside from the protonation (3) and chlorination (2) products in which cleavage of the aryl carbon-manganese bond occurs, one or both of two major organic derivatives (4) or (5) were isolated in all but the phenol reactions. Formation of both of these derivatives requires the initial insertion of CO



Scheme 4.6 (Compounds in italics not formed)

into the C-Mn bond. The insertion of CO into a metal-carbon bond under oxidative conditions has been discussed recently by Astruc.^[23] This electrocatalysis of CO insertion, demonstrated by Magnuson *et al*,^[23] is thought to be a result of the greater reactivity of 17-electron transition metal centres compared to their 18-electron counterpart. The fact that attempting the reaction under an atmosphere of CO had no noticeable effect on the product ratios or reaction rate suggests intramolecular insertion of CO. It should be noted that CO insertion into the aryl carbon-manganese bond was also observed in the reaction of $(\text{CO})_4\text{Mn}(\text{C}_6\text{H}_4\text{PPh}_2)$ with *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{PPh}_3$.^[24] Derivative (4) was isolated in all reactions, whereas (5) was only isolated when R was a methyl group.

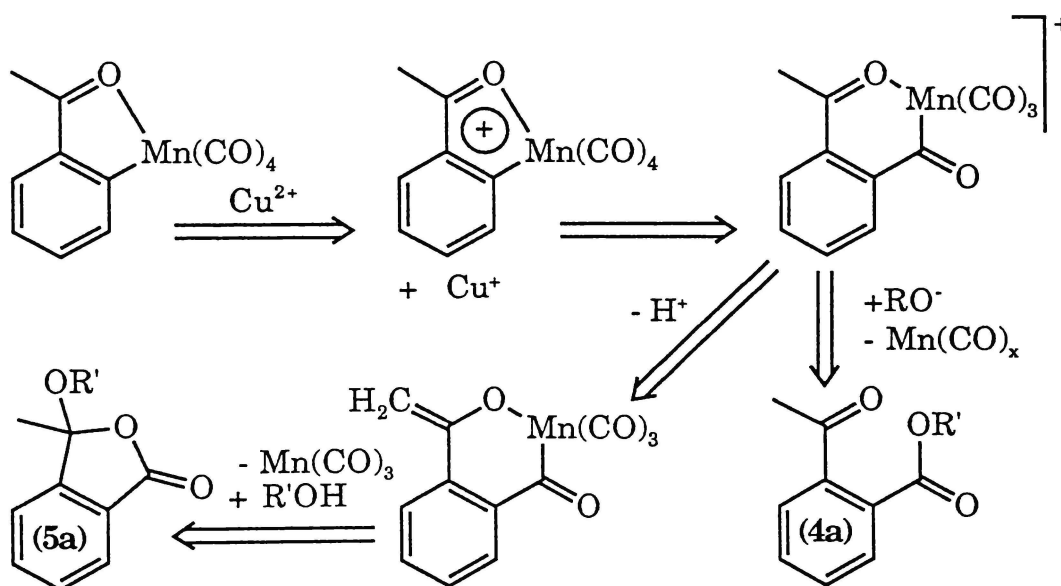


Scheme 4.7

Formation of the heterocyclic compound (5) incorporates the alkoxy group from the alcohol solvent and the R group on the same carbon atom. The most obvious mechanism for this would be formally nucleophilic attack of R'O^- at the carbon atom of the carbonyl function, followed by intramolecular nucleophilic attack of the ~~alkoxide-O~~ ^{alkoxide-O} at the carbon atom of the inserted carbonyl group with loss of the manganese moiety. If this

was the case then one would expect to isolate derivatives (5b) and (5c) also. While steric arguments may be used to account for the fact that benzophenone derivatives did not form a phthalide derivative, this does not account for the methoxy case. This suggests that the R substituent takes more than a passive role in the formation of (5).

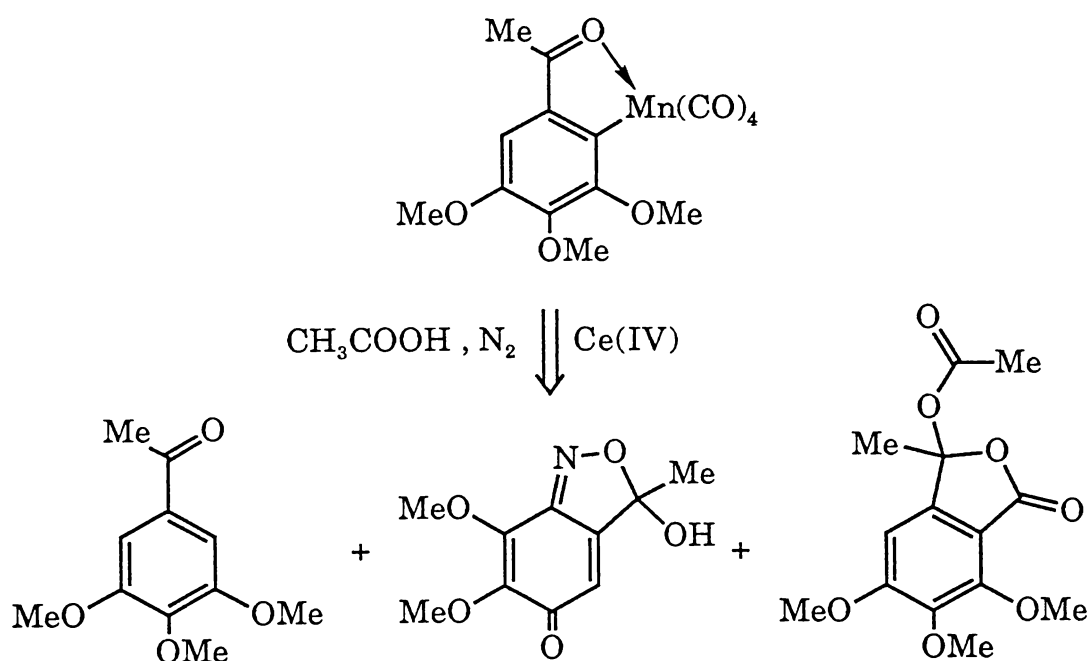
One major difference between (1a) and (1b),(1c) is the presence of a proton bonded to the α carbon in (1a) which is absent in both (1b) and (1c). This suggests involvement of the enol isomer of (1a) in the formation of the heterocycle followed by Markovnikov addition of a solvent molecule across the double bond of the resulting alkene as shown in Scheme 4.8.



Scheme 4.8

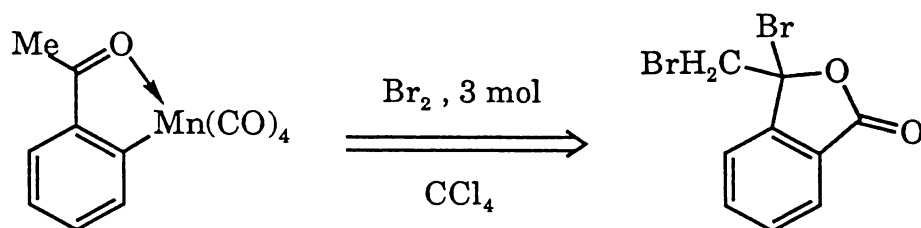
It is apparent from the above results that transmetallation, such as takes place between *ortho*-manganated ketones and mercury halides to give organomercury compounds, does not occur for CuCl_2 with *ortho*-manganated aryl ketones. Instead the $\text{Cu}(\text{II})$ acts as an oxidant facilitating CO insertion into the organocarbon-manganese bond followed by attack of a nucleophile, intramolecularly or by $\text{R}'\text{O}^-$ from the solvent, with elimination of the Mn functionality. This gives, in the case of $\text{R}'\text{O}^-$ attack, an ester function in the position previously occupied by the manganese group. Intramolecular attack is followed by loss of a proton

and addition of the solvent, HOR', across the double bond of the alkene to give a 3-alkoxy-3-methyl phthalide. In other oxidations of *ortho*-manganated aryl ketones the major products resulted from aryl carbon-manganese bond cleavage, not from CO insertion. The Ce(IV) oxidation of *ortho*-manganated aryl ketones in CD_3COOD lead to deuteration of the aryl ring with elimination of the manganese functionality.^[25] When a larger scale reaction using standard glacial acetic acid (Scheme 4.9) in place of the deuterated form was performed the major product was again the protonated ketone, however in this case significant amounts of a cyclic hemiketal and a small amount of a substituted phthalide were also isolated.



Scheme 4.9

Bromination and iodination were similarly achieved by oxidation with Br_2 or ICl respectively in CCl_4 .^[25] However, Schreiber Crawford found that the major product from the reaction of $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$ and a three fold excess of Br_2 in CCl_4 (Scheme 4.10) afforded as the major product the dibromide of vinylphthalide.^[26] This product can easily be rationalised in terms of Scheme 4.8 with addition of Br_2 across the double bond instead of MeOH .



Scheme 4.10

While the CuCl_2 oxidations of *ortho*-manganated aryl ketones in $\text{R}'\text{OH}$ do not lead to one product as in many of the above reactions, they are more predictable, with formation of ketoesters in all reactions and phthalide derivatives when the enol isomer of the ketone is available.

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Chapter Five

CHAPTER FIVE

REACTIONS OF ORTHO-METALLATED ARYL KETONES WITH PHOSPHORUS, ALUMINIUM AND TIN HALIDES

5.1 INTRODUCTION

As discussed in Section 4.1, *ortho*-manganated aryl ketones undergo transmetallation with HgCl_2 . While CuCl_2 did not behave analogously, the use of organomercury compounds in the synthesis of organometallics is well-known.^[1-3] This use of organomercury compounds, as transmetallation reagents, in the production of functionalised aryl complexes of gold,^[4-6] palladium,^[7,8] platinum,^[9] rhodium^[10,11] and tin,^[12] suggested that further study of the aryl transfer reactions of *ortho*-metallated aryl ketones was warranted.

In this chapter other potential aryl transfer reactions, with tin, aluminium and phosphorus, are discussed.

5.2 REACTION OF η^2 -(2-ACETYLPHENYL)TETRACARBONYLMANGANESE WITH Ph_2PCl

5.2.1 Preparation of *fac*- η^2 -(2-acetylphenyl)(chlorodiphenylphosphane)tricarbonylmanganese

A solution of 2-MeC($\overline{\text{O}}$) $\text{C}_6\text{H}_4\overline{\text{Mn}}(\text{CO})_4$ (0.461 g, 1.16 mmol) and PPh_2Cl (0.307 g, 1.39 mmol) in 40-60° petroleum spirits was refluxed for

48 hours. The solution was concentrated and cooled to give orange crystals of *fac*-[2-MeC($\overline{\text{O}}$)C₆H₄Mn(CO)₃(PPh₂Cl)] identified by an infrared spectrum $\nu(\text{CO})_{\text{CH}_2\text{Cl}_2}$ (2023 s, 1954 s and 1915 s) cm⁻¹ (see Section 5.2.3); and by FAB-MS (*m/e* 478 (*M*)⁺; *m/e* 450 (*M* - CO)⁺; *m/e* 443 (*M* - Cl)⁺; *m/e* 394 (*M* - 3CO)⁺ and *m/e* 359 (*M* - 3CO-Cl)⁺) (see Section 5.2.4).

5.2.2 Preparation of Mn₂(μ-η¹,η¹-Ph₂PPPh₂)(μ-Cl)₂(CO)₆

Further refluxing of a solution of *fac*-[2-MeC($\overline{\text{O}}$)C₆H₄Mn(CO)₃(PPh₂Cl)], prepared as in Section 5.2.1, for 6 days led to an orange solution. Removal of the solvent and recrystallisation of the residue from CH₂Cl₂/petroleum spirit, gave Mn₂(μ-η¹,η¹-Ph₂PPPh₂)(μ-Cl)₂(CO)₆ (0.136 g, 17 %) identified by infrared $\nu(\text{CO})_{\text{hexane}}$ (2058 s, 2042 m, 1996 s, 1969 m and 1934 m) cm⁻¹ (see Section 5.2.5); by an electron-impact mass spectrum (*m/e* 676, 592, 564, 535 and 480) (see Section 5.2.6); and by a full X-ray crystallographic determination (see Section 5.2.7).

Electron probe analysis of a crystal of Mn₂(μ-η¹,η¹-Ph₂PPPh₂)(μ-Cl)₂(CO)₆ gave an P : Cl : Mn ratio of 1.0 : 0.8 : 1.2. Within the accuracy of the technique this is in agreement with the 1 : 1 : 1 ratio expected for the complex.

5.2.3 Infrared Spectrum of *fac*-η²-(2-acetylphenyl)(chloro-diphenylphosphane)tricarbonylmanganese

The solution infrared spectrum in the $\nu(\text{CO})$ region of *fac*-[2-MeC($\overline{\text{O}}$)C₆H₄Mn(CO)₃(PPh₂Cl)] in dichloromethane exhibited three strong bands at 2023, 1954 and 1915 cm⁻¹. Comparison of this spectrum with those of well-characterised species such as *fac*-[2-MeC($\overline{\text{O}}$)C₆H₄Mn(CO)₃(PPh₃)]^[13] (2005 s, 1925 s and 1891 s) cm⁻¹ support the above formulation; the shift of *ca* 20 cm⁻¹ to higher frequencies is as expected when PPh₂Cl replaces PPh₃.

5.2.4 Mass Spectrum of *fac*- η^2 -(2-acetylphenyl)(chlorodiphenyl-phosphane)tricarbonylmanganese

The FAB mass spectrum of *fac*-[2-MeC($\overline{\text{O}}$)C₆H₄Mn(CO)₃(PPh₂Cl)] exhibits the molecular ion at m/e 478 along with other prominent peaks corresponding to $M - \text{CO}^+$ (m/e 450), $M - \text{Cl}^+$ (m/e 433), $M - 3\text{CO}^+$ (m/e 394), $M - 3\text{CO}-\text{Cl}^+$ (m/e 359).

5.2.5 Infrared Spectrum of Mn₂(μ - η^1 , η^1 -Ph₂PPPh₂)(μ -Cl)₂(CO)₆

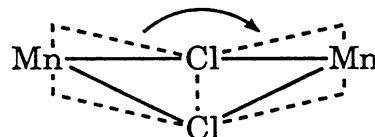
The solution infrared spectrum in the $\nu(\text{CO})$ region of Mn₂(μ - η^1 , η^1 -Ph₂PPPh₂)(μ -Cl)₂(CO)₆, recorded in hexane, corresponds well with those reported for the bromine and iodine analogues shown in Table 5.1, as well as their diarsane analogues. The increase in frequency of the individual bands in going from the iodo to the bromo derivative is found also in moving from the bromo to the chloro derivative.

Table 5.1 Infrared spectra of Mn ₂ X ₂ (CO) ₆ E ₂ Ph ₄ (E = P, As; X = Cl, Br, I) complexes in the $\nu(\text{CO})$ region.							
Compound	$\nu(\text{CO})$, cm ⁻¹						
Mn ₂ Cl ₂ (CO) ₆ As ₂ Ph ₄ ^a	2058 s	2042 m	-	1996 s	1969 m	1934 m	
Mn ₂ Br ₂ (CO) ₆ P ₂ Ph ₄ ^b	2052 s	2037 s	2018 w ^c	1971 s	1966 m	1931 m	[14]
Mn ₂ Br ₂ (CO) ₆ As ₂ Ph ₄ ^b	2049 s	2034 vs	2019 w ^c	1970 s	1964 m	1933 m	[14]
Mn ₂ I ₂ (CO) ₆ P ₂ Ph ₄ ^b	2041 s	2027 vs	2012 w ^c	1966 s	-	1930 m	[14]
Mn ₂ I ₂ (CO) ₆ As ₂ Ph ₄ ^b	2040 s	2026 vs	2012 w ^c	1966 s	-	1933 m	[14]
^a In hexane. ^b In CCl ₄ . ^c Attributed to ¹³ CO.							

For Mn₂(μ - η^1 , η^1 -Ph₂EEPh₂)(μ -X)₂(CO)₆ (E = P, As; X = Cl, Br, I) complexes, C_{2v} is the highest expected symmetry in solution for the Mn₂(CO)₆ fragment. This gives an irreducible representation for the carbonyl stretching modes of 2A₁ + A₂ + 2B₁ + B₂. This predicts 5 infrared active modes (the A₁, B₁ and B₂). The observed spectra for the chlorine and bromine analogues have all the bands predicted for C_{2v} with only four bands observed in the CCl₄ solution infrared spectrum of the iodine analogues. The lower number of observed bands can be attributed to

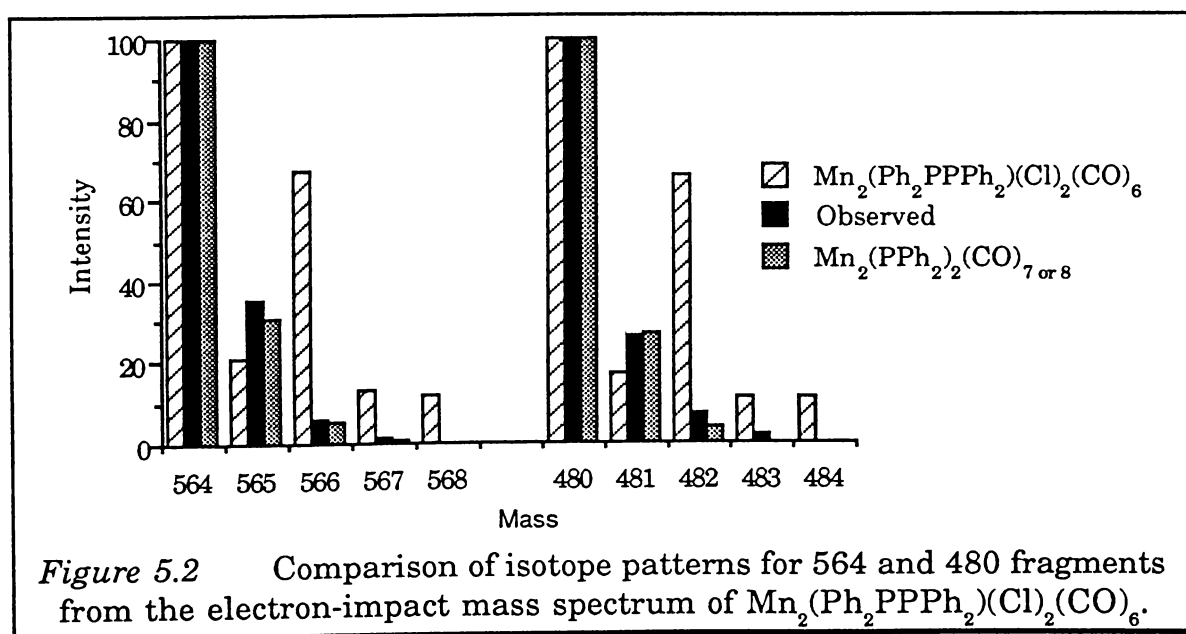
coincidental overlap of some fundamentals. It had been noted earlier^[15] that for the series of similar Te_2Ph_2 complexes of rhenium and manganese all five bands were observed for the complexes with smaller dihedral angles (see Figure 5.1) and only four for larger dihedral angles. It is believed that removal of the accidental degeneracy of two of the infra-red modes is favoured by small dihedral angles, as a consequence of better coupling between the two $\text{M}(\text{CO})_3$ groups.

Figure 5.1 The dihedral angle between the planes defined by the equatorial ligands about each manganese atom.



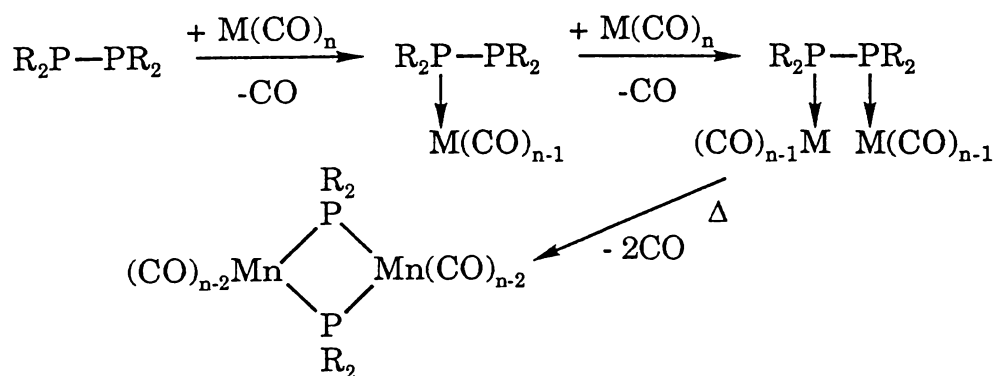
5.2.6 Mass Spectrum of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$

An electron-impact mass spectrum of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$, with envelopes at m/e 676, 592, 564, 535 and the base peak at 480, was not consistent with the above formulation. While the envelopes at 564 and 480 would be expected as the molecular ion and $M - 3\text{CO}^+$ for $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ the $M + 2$ peaks were nowhere near as large as would be expected for a species which contained two chlorine atoms (see Figure 5.2).



Other envelopes with 100 % peaks at m/e 676, 592, 564, and 480, when assigned in terms of $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$, correspond to fragments of $M\text{-CO}^+$, $M\text{-4CO}^+$, $M\text{-5CO}^+$ and $M\text{-8CO}^+$, respectively. This initially misleading spectrum suggested the structure $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_{7\text{ or }8}$ and breakdown fragments therefrom. However the infrared spectrum was inconsistent with both of these species so an X-ray structure determination was performed. This confirmed the compound to be $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ as suggested by infrared.

The anomalous mass spectrum can be explained in terms of decomposition at the probe temperatures giving $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$ which then dominates the spectrum. This decomposition is supported by the fact that it has been shown^[14] that the bromine and iodine analogues of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ rearrange thermally to give $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$; and by the thermal formation of $(\mu\text{-PPh}_2)$ bridged species in many cases when simple carbonyl substitution is the aim^[16-22] (see Scheme 5.1). Indeed this is the reason why complexation reactions induced by thermal activation are often forsaken for milder reactions, like irradiation.^[23-26]



Scheme 5.1

Table 5.2 Crystal data for $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$.

Molecular formula : $\text{C}_{30}\text{H}_{20}\text{Cl}_2\text{Mn}_2\text{O}_6\text{P}_2$

M = 719.22

Crystal class : Triclinic

Space group : $\text{P}\bar{1}$

a = 10.908(4) *α* = 96.20(2)

b = 11.756(3) *β* = 99.51(2)

c = 12.186(3) *γ* = 96.56(2)

U = 1518.2(8) *F*(000) = 720

Z = 2 *D*_{calc} = 1.57 g cm⁻³

X-rays : Mo-K_α (λ = 0.710 73 Å)

Temperature of collection : -110°C

Linear absorption coefficient (μ) : 9.7 cm⁻¹

5.2.7 X-ray Structure Determination of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$

5.2.7.1 Data collection

Orange, rectangular shaped crystals were grown from a solution in CH_2Cl_2 /hexane, which had been cooled to -10°C from room temperature.

One of the well-formed crystals was attached to a fine glass fibre with grease and mounted on a goniometer. Preliminary precession photography indicated a space group of P1 or $\text{P}\bar{1}$.

The same crystal, of dimensions 0.26 x 0.16 x 0.08 mm, was sent to the University of Canterbury for intensity data collection. Using a Nicolet P3 diffractometer with zirconium filtered Mo-K_α radiation a total of 3908 unique reflections were collected within the range of 4° < 2θ < 45°. Data

were collected in $P\bar{1}$ with $a = 10.980(4)$, $b = 11.756(3)$ and $c = 12.186(3)$ Å, $\alpha = 96.20(2)$, $\beta = 99.51(2)$ and $\gamma = 96.56(2)^\circ$; $U = 1518.2(8)$ Å³ and $Z = 2$. The crystal data are given in Table 5.2. After correction for Lorentz, polarisation and absorption (based on ϕ -scans) effects, 1502 data had $I > 3.0\sigma(I)$ and were used in all calculations.

5.2.7.2 Solution and refinement

The structure was solved using the TREF direct method routine of SHELXS86^[27] and routinely developed using SHELX-76^[27] for the calculations. In the final cycles of least-squares refinement the manganese, phosphorus and chlorine atoms were assigned anisotropic temperature factors, while other atoms were modelled isotropically. Phenyl rings were included as rigid hexagons with hydrogen atoms in calculated positions fixed at 98 pm from the attached carbon atom.

After introduction of a weighting scheme the refinement converged to give $R = 0.0808$ with $R_w = 0.0820$ and $w = (\sigma^2(F) + 0.003\ 06F^2)^{-1}$. The final difference map showed some residual electron density of $ca. 0.9\ e\ \text{\AA}^{-3}$ near one of the chlorine atoms. This can be attributed to difficulties with absorption corrections. No parameter shifted by more

Table 5.3 Comparison of the bond parameters for $Mn_2(\mu-\eta^1, \eta^1-Ph_n EEP_h_n)(\mu-X)_2(CO)_6$, distances in pm and angles in degrees.									
E	X	Mn...Mn	Mn-X ^a	Mn-E ^a	E-E	Mn-E-E ^a	Mn-X-Mn ^a	X-Mn-X ^a	Fold ^c Angle
P	Cl	353.3	241.1(6)	236.6(7)	233.5(3)	104.4(3)	94.2(2)	84.6(2)	15.1
P	Br ^b	366.1	253.3(2)	235.5(4)	232.2(4)	106.4(2)	92.5(1)	85.4(1)	21.0
P	I ^b	386.3	271.8(2)	236.2(3)	233.3(4)	108.7(2)	90.5(1)	84.4(1)	31.5
As	Br ^b	370.7	254.0(6)	245.6(6)	248.9(5)	104.3(2)	93.8(2)	85.1(2)	15.8
Se	Br ^d	368.0		247.8(3)	240.1(3)				12.3
Te	Br ^d	365.9		246.2(7)	279.5(5)				10.7
^a Average values given. ^b Taken from Ref. 14. ^c The dihedral angle between the planes defined by the equatorial ligands about each manganese atom, taking the phosphorus atoms as axial. ^d Taken from Ref. 28.									

than two percent of its estimated standard deviation in the final refinement cycle.

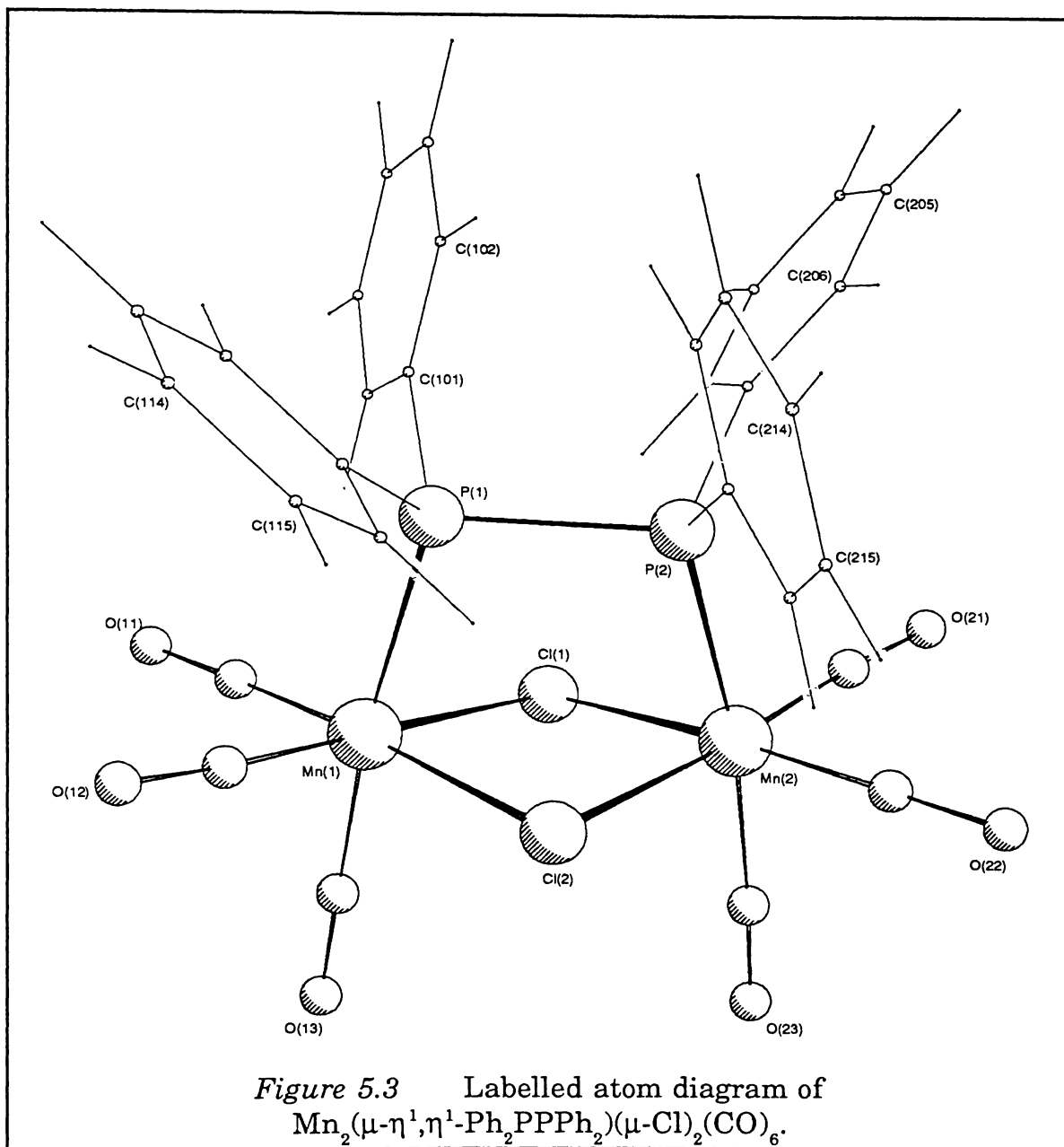
Selected bond lengths and angles are compared in Table 5.3 with those of the bromine and iodine analogues, all bond lengths and angles, the final positional parameters and final thermal parameters in Appendix 7. A labelled atom diagram is shown in Figure 5.3, with perspective views in Figures 5.4 and 5.5.

5.2.7.3 Discussion of the structure of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$

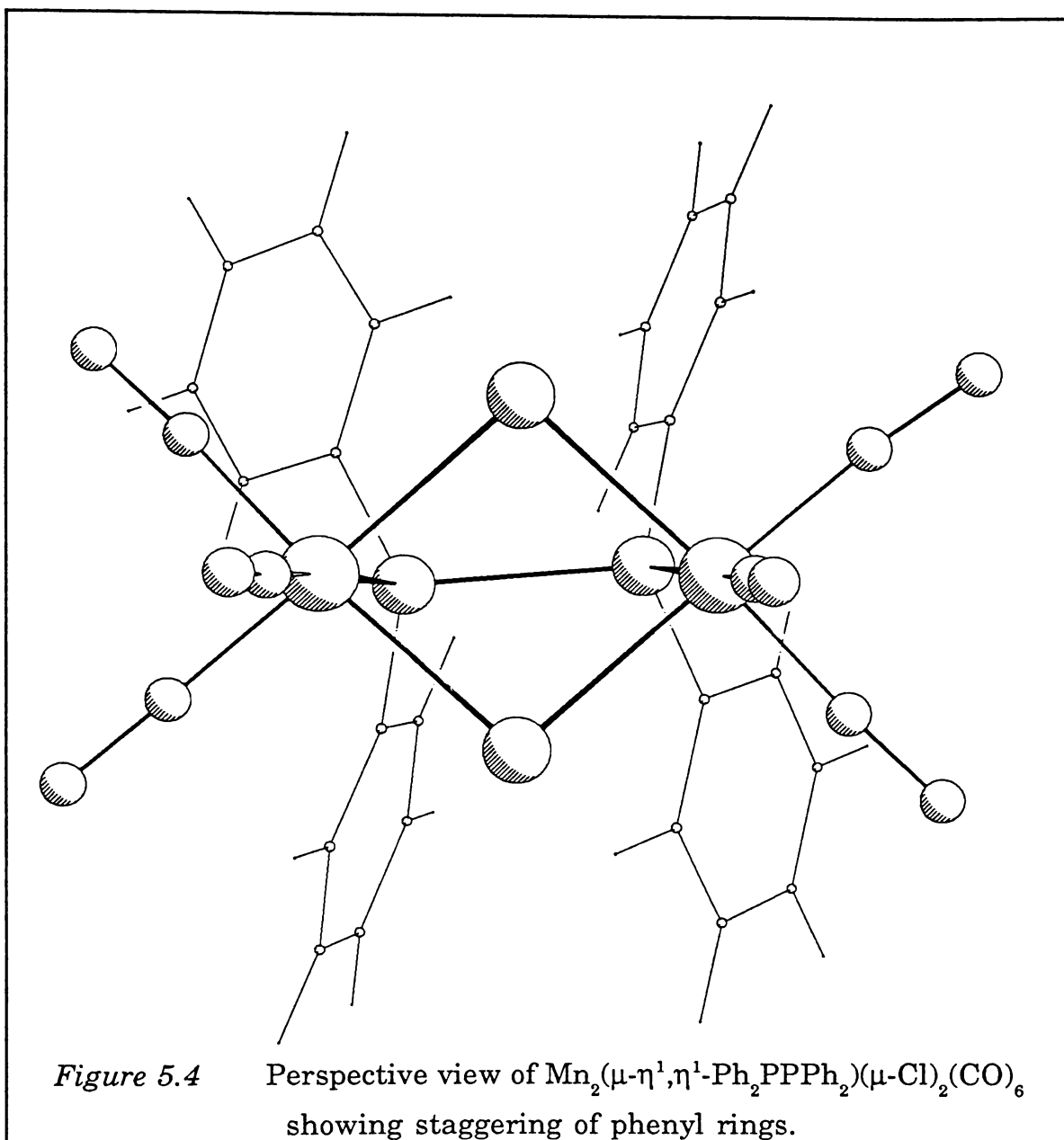
The structure as illustrated in Figure 5.3 consists of discrete molecules each of which contain two pseudo-octahedral manganese(I) surrounded by three *fac*-carbonyl ligands, two *cis*-chlorides and one of the phosphorus donor atoms of the $\text{Ph}_2\text{P-PPh}_2$ ligand. As is found for other isostructural compounds $\text{M}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_n\text{EPh}_n)(\mu\text{-X})_2(\text{CO})_6$ ($\text{M} = \text{Mn}^{[29]}$ or $\text{Re}^{[30]}$ $\text{X} = \text{Br}$, $n = 2$, $\text{E} = \text{P}$; $\text{M} = \text{Re}^{[15,31,32]}$ $\text{X} = \text{Br}$ or I , $n = 1$, $\text{E} = \text{S}$, Se or Te ; $\text{M} = \text{Mn}^{[28]}$ $\text{X} = \text{Br}$, $n = 1$, $\text{E} = \text{Se}$ or Te ; $\text{M} = \text{Mn}^{[14]}$ $\text{X} = \text{Br}$, $n = 2$, $\text{E} = \text{As}$; $\text{M} = \text{Mn}$, $\text{X} = \text{I}^{[14]}$ or $\text{Cl}^{[33]}$ $n = 2$, $\text{E} = \text{P}$; $\text{M} = \text{Re}^{[34]}$ $\text{X} = \text{Br}$, $n = 2$, $\text{E} = \text{P}$, As or Sb), the two octahedra are joined by a common edge along the $\text{Cl}\dots\text{Cl}$ vector in such a way that the two $\text{Mn}(\text{CO})_3$ fragments are joined by two bridging chloride ligands, with a bidentate $\text{Ph}_2\text{P-PPh}_2$ bridge further linking the two metal atoms together.

The average Mn-Cl distance found for $\text{Mn}_2(\text{Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ is 241.1(6) pm. This is marginally longer than those observed for hexacoordinated manganese compounds with bridging chlorides, such as $\text{Mn}_2\text{Cl}_2(\text{CO})_8$ for which distances of 239.4(1)-239.6(1) pm were reported by Clegg and Morton^[35] and of 234.7(4)_{av} pm by Greene and Bryan.^[36] It should be noted that the Mn-Br distances in $\text{Mn}_2(\text{Ph}_2\text{PPPh}_2)(\mu\text{-Br})_2(\text{CO})_6$ (253.4(2)_{av} pm)^[14] are also observed to be slightly longer than for $\text{Mn}_2\text{Br}_2(\text{CO})_8$ (251.4(9)-253.4(10) pm)^[37] Comparison of the Mn-X distances

of $\text{Mn}_2(\text{Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ with those of the bromine and iodine^[14] (271.8(2)_{av} pm) analogues shows the expected increase in moving down the group from Cl to I.

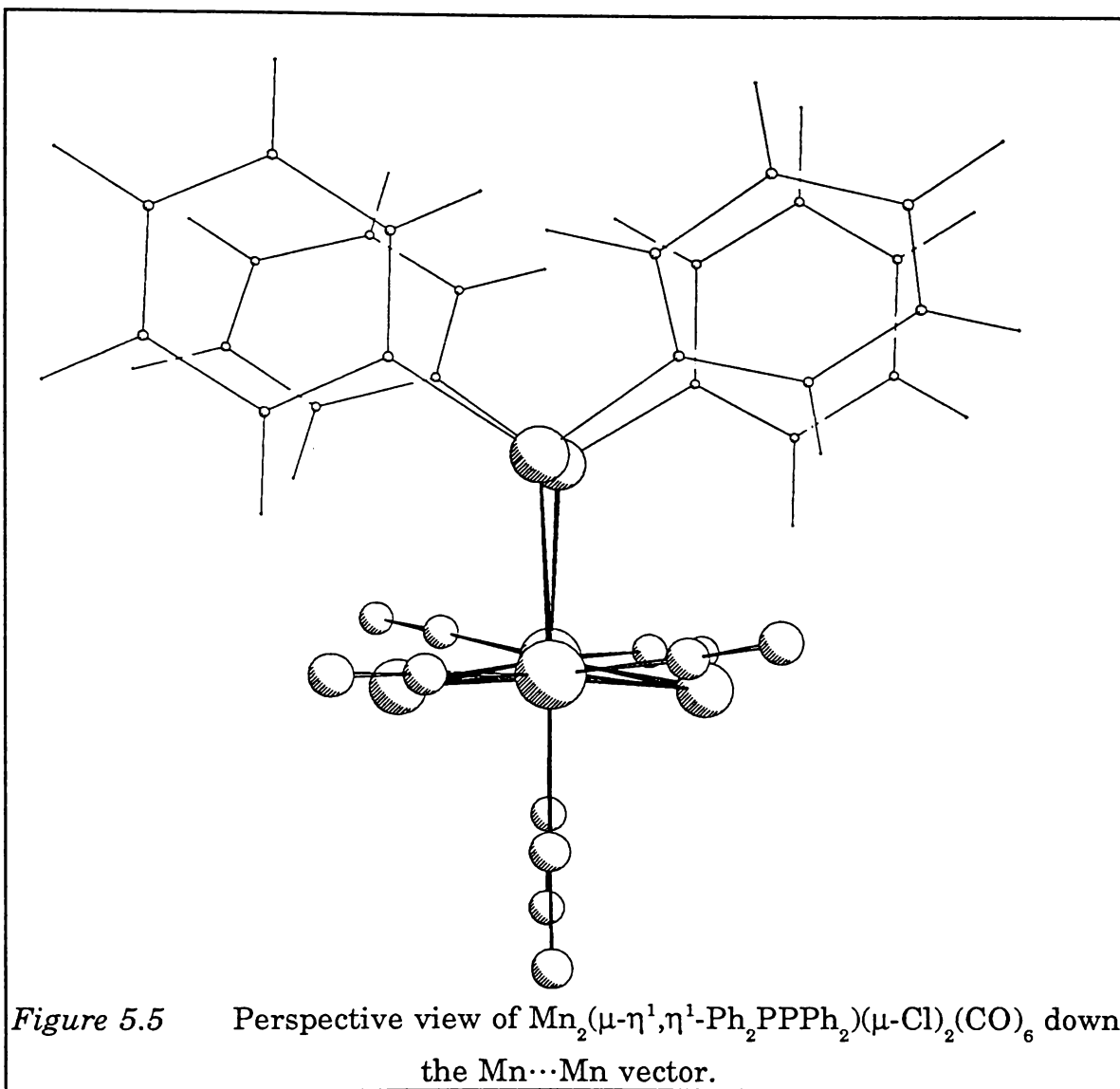


The P-P bond distance of 233.5(3) pm, while essentially identical to those found for the Br (232.2(4) pm) and I (233.3(4) pm) analogues, is some 10 pm longer than the 219.2(9) pm^[38] observed for uncomplexed P_2Me_4 . This is somewhat similar to what has been observed earlier for similar molecules with chalcogens as ligands such as $\text{Mn}_2(\text{PhEEPh})(\mu\text{-Br})_2(\text{CO})_6$ ^[28] and $\text{Re}_2(\text{PhEEPh})(\mu\text{-Br})_2(\text{CO})_6$ ^[15,31,32] (E = S, Se



or Te). There is also little variation in the Mn-P bond lengths between the Cl ($236.6(7)_{\text{av}}$ pm), Br ($235.5(4)_{\text{av}}$ pm) and I ($236.2(3)_{\text{av}}$ pm) analogues.

Comparison of the Mn...Mn non-bonding distances found in the chlorine (353.3 pm) analogue prepared in this study and those of the bromine (366.1 pm) and iodine (386.3 pm) show a general increase correlating with the bridging halide atoms size. The presence of the bridging diphosphane does not have a marked effect on this non-bonding



distance. The corresponding lengths found for the $\text{Mn}_2\text{X}_2(\text{CO})_8$ complexes are in agreement at 356.9 and 374.3 pm respectively.

The Mn-C distances for $\text{Mn}_2(\text{Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ (range 176(2) to 186(2) pm), the carbonyl ligand C-O bond distances (range 113(3) to 121(2) pm) and the P-C bond distances (183(1) to 187(1) pm) are normal.

The Mn-P-P bond angles for $\text{Mn}_2(\mu\text{-}\eta^1,\eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ of $104.4(3)^\circ_{\text{av}}$ are more acute than those observed for the bromine analogue ($106.4(2)^\circ_{\text{av}}$), which are in turn more acute than those of the iodine analogue ($108.7(2)^\circ_{\text{av}}$). This opening of the Mn-P-P bond as the bridging

halide increases in size is not surprising as the P-P and Mn-P bond distances are relatively constant going down Group 17 whereas the Mn...Mn distance increased. The Cl-Mn-Cl bond angles of $84.6(2)^\circ_{\text{av}}$, while not the ideal (90°), are essentially the same as those found for a wide range of dihalide bridged dimanganese complexes (range from $83.7(1)$ to $85.4(1)^\circ$).

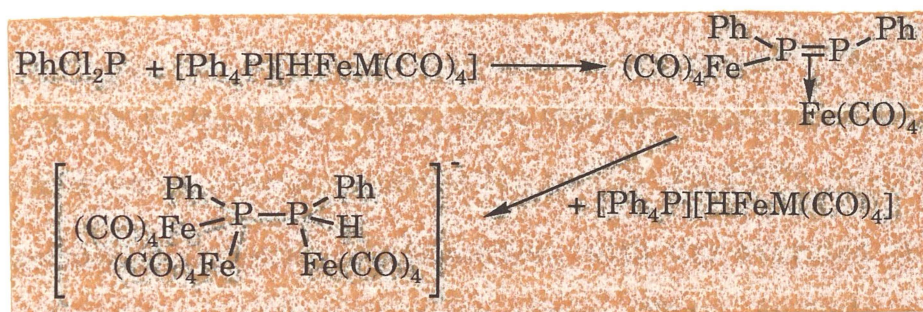
The 'fold angle', as described in Table 5.3, for $\text{Mn}_2(\text{Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ of 15.1° is smaller than those observed for the bromine (21.0°) and iodine (31.5°) analogues. The increase in 'fold angle' as the bridging halide increases in size contrasts the trend observed when the steric bulk of the E ligand is increased; the 'fold angle' observed for $\text{Mn}_2(\text{Ph}_2\text{AsAsPh}_2)(\mu\text{-Br})_2(\text{CO})_6$ of 15.8° is smaller than observed for the phosphorus analogue.

5.2.8 Discussion

The initial reaction between $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$ and PPh_2Cl involves CO replacement to give *fac*- $[2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_3(\text{PPh}_2\text{Cl})]$ in essentially quantitative yield. This assignment is based on a FAB mass spectrum, and on the similarity of the $\nu(\text{CO})$ pattern to that of well-characterised species such as *fac*- $[2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_3(\text{PPh}_3)]$. Thermal reactions between cyclometallated ketones and phosphanes are known to give direct substitution of a CO ligand rather than displacement of the coordinated oxygen atom.^[13,39]

Prolonged refluxing of this first-formed species gave an orange solution from which $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ was isolated as a major product. An electron-impact mass spectrum of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ was misleading in that the only peaks observed corresponded to $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_{7 \text{ or } 8}$ and breakdown fragments therefrom, but the infrared spectrum was inconsistent with these species so full characterisation by X-ray crystallography was undertaken. The

structure is illustrated in Figure 5.3, and consists of two $\text{Mn}(\text{CO})_3$ fragments joined by two bridging chloride ligands, with a $\text{Ph}_2\text{P}-\text{PPh}_2$ group further linking the two metal atoms together. The bromine and iodine analogues of $\text{Mn}_2(\mu-\eta^1, \eta^1-\text{Ph}_2\text{PPPh}_2)(\mu-\text{Cl})_2(\text{CO})_6$ have been prepared previously by direct reaction of preformed $\text{Ph}_2\text{P}-\text{PPh}_2$ with the appropriate $\text{XMn}(\text{CO})_5$ species,^[14] but the synthesis reported here is novel in that the diphosphane ligand is assembled in the reaction system. Diphosphane ligands have been synthesised in a similar way by reaction of PhPCl_2 with $[\text{Ph}_4\text{P}][\text{HFe}(\text{CO})_4]$ to give $\{\text{Fe}(\text{CO})_4[\mu-\text{Fe}(\text{CO})_4](\text{PPh})_2\}$. Further reaction of $\{\text{Fe}(\text{CO})_4[\mu-\text{Fe}(\text{CO})_4](\text{PPh})_2\}$ with $[\text{Ph}_4\text{P}][\text{HFe}(\text{CO})_4]$ affords the trimetallic anionic complex $[\text{Ph}_4\text{P}]\{[\text{Fe}(\text{CO})_4]_2(\text{Ph})\text{PP}(\text{Ph})(\text{H})[\text{Fe}(\text{CO})_4]\}^{[40]}$ as shown in Scheme 5.2. It has also been shown^[14] that the bromine and iodine analogues of $\text{Mn}_2(\mu-\eta^1, \eta^1-\text{Ph}_2\text{PPPh}_2)(\mu-\text{Cl})_2(\text{CO})_6$ rearrange thermally to give $\text{Mn}_2(\mu-\text{PPh}_2)_2(\text{CO})_8$. This explains the anomalous mass spectrum of $\text{Mn}_2(\mu-\eta^1, \eta^1-\text{Ph}_2\text{PPPh}_2)(\mu-\text{Cl})_2(\text{CO})_6$; clearly decomposition at the probe temperatures gave $\text{Mn}_2(\mu-\text{PPh}_2)_2(\text{CO})_8$ which then dominates the spectrum.



Scheme 5.2

The mechanism of formation is as yet unclear. The first-formed species is *fac*-[2-MeC($\bar{\text{O}}$)C₆H₄Mn(CO)₃(PPh₂Cl)] and this subsequently rearranges to $\text{Mn}_2(\mu-\eta^1, \eta^1-\text{Ph}_2\text{PPPh}_2)(\mu-\text{Cl})_2(\text{CO})_6$. The fate of the organic fragment is not known but it is probably lost as acetophenone by abstraction of a hydrogen atom from the solvent. A migration of the chlorine from phosphorus to manganese followed by dimerisation of two

$\text{ClMn}(\text{PPh}_2)(\text{CO})_3$ fragments would give the final product. Another route would involve the oxidative addition of a P-Cl bond of a coordinated ligand to a second manganese centre. This seems less likely as it would form species with $\mu\text{-PPh}_2$ moieties and, as mentioned above, compounds of this type have been shown^[14] to be intermediates in the formation of $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$ complexes from compounds of the type $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-X})_2(\text{CO})_6$ ($\text{X} = \text{Br}, \text{I}$); it therefore seems unlikely that two $\mu\text{-PPh}_2$ moieties would revert to a $\text{Ph}_2\text{P-PPh}_2$ ligand. It should be noted that oxidative addition of the P-Cl bond of PPh_2Cl to a molybdenum centre, with subsequent P-C bond formation, has been observed.^[41] Other examples of P-C and indeed P-P bond formation are illustrated by the reactions of CH_2I_2 with carbonyl and nitrosyl diiron phosphanes.^[42] The reaction of $[(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)(\mu\text{-CO})\text{Fe}(\text{CO})_2(\text{PPh}_2)]^{2-}$ with CH_2I_2 affords as the neutral species $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)(\mu\text{-}\eta^1, \eta^1\text{-H}_2\text{CPh}_2)\text{Fe}(\text{CO})_3$ ^[43] and a similar reaction using $[(\text{NO})_2\text{Fe}(\mu\text{-PPh}_2)(\mu\text{-NO})\text{Fe}(\text{NO})(\text{PPh}_2)]^{2-}$ affords the corresponding nitrosyl as well as the diphosphino derivative $(\text{NO})_2\text{Fe}(\mu\text{-CH}_2)(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)\text{Fe}(\text{NO})_2$.^[44]

Comparison of the major structural features of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ with the corresponding features in its bromine and iodine analogues shows $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ to adopt essentially the same conformation, with the expected changes to accommodate the smaller halogen atoms. These include a shorter $\text{Mn}\cdots\text{Mn}$ distance, and more acute Mn-P-P and Mn-X-Mn angles as X goes from I through Br to Cl . The 'fold angle' between the two tetragonal planes also decreases so that the Ph_2PPh_2 ligand maintains a constant geometry in all three complexes.

5.3 REACTION OF η^2 -(2-ACETYLPHENYL)TETRACARBONYLMANGANESE WITH AlCl_3

A solution of $2\text{-MeC}(\text{O})\overline{\text{C}_6\text{H}_4}\text{Mn}(\text{CO})_4$ (0.829 g, 2.9 mmol) in toluene (10 ml) was added to freshly sublimed AlCl_3 (0.386 g, 2.9 mmol) in a Schlenk tube. The mixture was refluxed under N_2 and the disappearance of the starting material monitored by infrared spectroscopy. The solution initially went orange then back to yellow. After 4 hours spectroscopic evidence suggested 95 % conversion to a second species: $\nu(\text{CO})_{\text{toluene}}$ (2045 s, 2011 vs and 1983 s,br) cm^{-1} . The mixture was allowed to settle, the yellow solution syringed off under N_2 and the toluene removed on a rotary evaporator. This left a mixture consisting of a colourless liquid, pale yellow needles and yellow-orange blobs. A few of the pale yellow needles were removed for X-ray crystal analysis (see Section 5.3.1), the remainder dissolved in a minimal amount of dichloromethane (ca. 10 ml) to which silica gel (2-3 g) was added. Removal of the solvent afforded a pale yellow powder (consisting of the silica with adsorbed products) which was added to the top of a silica gel column (2 x 8 cm). Elution with 40-60° petroleum-spirits gave yellow $\text{Mn}_2(\text{CO})_{10}$, identified by infrared spectroscopy $\nu(\text{CO})_{\text{hexane}}$ (2046 s, 2015 vs and 1984 s) cm^{-1} and with 40-60° petroleum-spirits/dichloromethane 1:1 gave two bands: (i) $2\text{-MeC}(\text{O})\overline{\text{C}_6\text{H}_4}\text{Mn}(\text{CO})_4$ $\nu(\text{CO})_{\text{hexane}}$ (2083 m, 1995 vs and 1947 s) cm^{-1} and (ii) $\text{MeC}(\text{O})\text{Ph}$ mass spectrum (m/e 120 M^+ , m/e 105 ($\text{M}-\text{Me}$) and m/e 77 ($\text{M}-\text{COMe}$)).

5.3.1 Attempted X-ray Structure Analysis of Yellow Needles

One of the well-formed yellow needles, obtained from the reaction mixture, was attached to a fine glass fibre with grease and mounted on a goniometer. The crystals decomposed in the X-ray beam at room temperature such that only five or six photos could be taken. However, preliminary precession photography on a number of crystals indicated a space group of P1 or $\text{P}\bar{1}$.

Crystals sent to the University of Canterbury were collected in $P\bar{1}$ with $a = 5.89$, $b = 8.25$ and $c = 13.31$ Å, $\alpha = 68.7$, $\beta = 77.4$ and $\gamma = 79.5^\circ$; $U = 578.2$ Å³. However, most likely because of an incorrect unit cell, the structure would not solve using the TREFF direct method or PATT routines of SHELXS86.^[27] Hence, the data were recollected in space group C2 (space group selected by automatic cell search on the diffractometer) with $a = 23.903$, $b = 5.906$ and $c = 8.467$ Å, $\beta = 103.48^\circ$; $U = 1162.4$ Å³. Once again the structure would not solve and so the data were transformed to other likely space groups to attempt to effect a solution, but in all cases (Cm, Cc, $C_{2/m}$, $C_{2/c}$, P1 and $P\bar{1}$) without success.

5.3.2 Discussion

Acetophenone and $Mn_2(CO)_{10}$ were the only products isolated from column chromatography of the reaction mixture from the reaction of $AlCl_3$ with $2-MeC(\bar{O})C_6H_4Mn(CO)_4$. Both these products were identified spectroscopically. Also isolated from the crude reaction mixture were some yellow crystals whose solution infrared spectrum was identical to that of $Mn_2(CO)_{10}$.

Crystal structure data collected from these crystals would not solve. However a unit cell size was obtained. If the compound was $Mn_2(CO)_{10}$ then a density of 1.11 g cm⁻³ would be the result for $Z = 2$ or twice that for $Z = 4$. A density of 2.22 g cm⁻³ seems unlikely considering $\rho = 1.83$ g cm⁻³ was found for $Mn_2(CO)_{10}$ in a previous structure determination.^[45] This suggests that some other species has co-crystallised with the manganese carbonyl. The only other species present were the toluene solvent and $AlCl_3$. The presence of one or two of these molecules per unit cell is unlikely as densities of 1.23 , 1.36 and 1.48 g cm⁻³ for the respective formulations $[Mn_2(CO)_{10}]_2 \cdot MePh$, $[Mn_2(CO)_{10}]_2 \cdot 2(MePh)$ and $[Mn_2(CO)_{10}]_2 \cdot 2(AlCl_3)$ seem low for this type of compound. Using the approximation that each non-hydrogen atom occupies 18 Å³ one would

expect 64 atoms in the unit cell. For $Z = 2$ this would give 32 atoms per independent unit, less 22 for $\text{Mn}_2(\text{CO})_{10}$ leaves 10 additional atoms. This could correspond to one AlCl_3 and one toluene molecule.

Two factors indicate the possibility of co-crystallisation of AlCl_3 with the $\text{Mn}_2(\text{CO})_{10}$: the first being that the evaporation of the solvent from a toluene solution of $\text{Mn}_2(\text{CO})_{10}$ leads to an amorphous yellow solid not to the needle shaped crystals which are observed when the toluene is evaporated from a toluene solution of $\text{Mn}_2(\text{CO})_{10}$ containing AlCl_3 ; and the second being the existence of other aluminium halide adducts of both metal and organic carbonyls. Examples of these types of adducts include $\text{Br}_3\text{Al}\cdot\text{Co}_2(\text{CO})_8$,^[46] $[\text{Me}(\text{Br}_2\text{BrAlO})\text{C}]\text{Mn}(\text{CO})_3$,^[47] and $\text{Cl}_3\text{Al}\cdot\text{OC}(\text{NMe}_2)_2$,^[48] along with the many others discussed by Horwitz and Shriver.^[49]

From the limited data available it appears that a different from $\text{Mn}_2(\text{CO})_{10}$ was isolated as the yellow needles. From density and cell volume considerations it appears that atoms in addition to those contributed by $\text{Mn}_2(\text{CO})_{10}$ are within the lattice. The requirement of the presence of AlCl_3 in the formation of these crystals suggests the presence of AlCl_3 groups in the lattice, either as independent molecules or as adducts of $\text{Mn}_2(\text{CO})_{10}$. However, without more data, the definite assignment of this structure is precluded.

5.4 REACTIONS OF ORTHO-METALLED ARYL KETONES WITH TIN HALIDES

In contrast to the reaction of aryllithium reagents with tin species, which afford polyaryltin compounds, arylmercury compounds give only mono- or di-aryl species.^[11,50] A number of different methods have been employed in the production of aryltin(IV) species including the reaction of tin(IV) halides with Schiff's bases.^[51] However more extensive chemistry has resulted from their preparation from the corresponding arylmercury compounds. These include redox transmetallation reactions^[12,52,53] using

tin metal or tin(II) halides with organomercury halides or transmetallation reactions^[52,53,54] using aryltin(IV) halides with diorganomercury complexes.

Formation of aryl-tin compounds with ketone functionalities is not possible by the above routes, due to the reactivity of the ketone group. A method for the formation of such species was sought as these species are of interest to gauge the degree of interaction of the *ortho*-oxygen atom with the metal, giving increased coordination numbers for the metal as the Lewis basicity of the metal centre increases. For example, one would expect less O...Sn interaction in going from η^2 -(2-acetylphenyl)trichlorotin(IV) to (2-acetylphenyl)trimethyltin(IV).

5.4.1 Attempted Symmetrisation of (2-acetylphenyl)chloromercury(II)

A common method used for the symmetrisation of RHgX compounds is to stir the halo-organomercury compound with an excess of KI in methanol or aqueous methanol.^[55]

A saturated solution of KI (0.36 g, 2.2 mmol) in dry MeOH was added to 2-MeC(O)C₆H₄HgCl (0.35 g, 1.0 mmol). The mixture was stirred at room temperature until all the 2-MeC(O)C₆H₄HgCl had dissolved and then for a further 10 minutes. Water was added until no more precipitate formed, the mixture filtered on a Buchner funnel, washed with water (3 x 20 ml) and air dried. The white precipitate was dissolved in a minimum of dichloromethane. To this was added a equal volume of 30-40° petroleum-spirits and the solution kept at -30° for two days. The white solid was filtered and air dried to give 2-MeC(O)C₆H₄HgI (0.182 g, 41 %), m.p. 154-156° (Found: H 1.47 and C 21.57; C₈H₇OHgI calculated: H 1.58, C 21.51, O 3.58, I 28.41 and Hg 44.91 %); FAB mass spectrum *m/e* 448 M⁺ and 321 (*M* - I)⁺; ¹H nmr (CDCl₃) (δ 8.10 Ar-H *dd* 1H, 7.68 Ar-H *ddd* 1H, 7.51 Ar-H *dd* 1H, 7.45 Ar-H *ddd* 1H and 2.70 -C(O)CH₃ *s* 3H) (see

Section 5.4.1.1) and ^{13}C nmr (CDCl_3) (δ 201.1 -C(O)- s, 159.4 -C_{Ar}Hg- s, 141.2 -C_{Ar}C(O)- s, 137.3 C_{Ar} d, 134.3 C_{Ar} d, 131.5 C_{Ar} d, 128.7 C_{Ar} d, and 27.1 -C(O)CH₃ q) (see Section 5.4.1.1).

5.4.1.1 ^1H and ^{13}C nmr spectroscopy of (2-acetylphenyl)iodomercury(II)

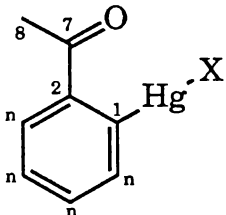
The ^1H and ^{13}C nmr spectra of 2-MeC(O)C₆H₄HgI were measured in CDCl_3 . The ^1H nmr spectrum consists of four single proton signals in the aryl region centred at δ 8.10, 7.68, 7.51 and 7.45 with two doublet of doublets ($1 \times {}^3\text{J}$ and $1 \times {}^4\text{J}$) and two doublet of doublet of doublets ($2 \times {}^3\text{J}$ and $1 \times {}^4\text{J}$) indicating a 1,2-disubstituted benzene ring. The remaining three proton signal, a singlet at δ 2.70, can be compared to δ 2.73 observed for the chloro analogue in d₆-acetone.^[13]

The ^{13}C nmr spectrum is also consistent with formulation as a 1,2-disubstituted aryl ketone, with singlet signals at δ 201.1 for the carbonyl carbon, 159.4 for aryl carbon directly bonded to the mercury atom, 141.2 for aryl carbon bonded to the carbonyl carbon and 27.1 for the methyl carbon atom. Four doublet carbon atoms were observed in the aryl carbon region at δ 137.3, 134.3, 131.5 and 128.7. As shown in Table 5.4, this is in good agreement with the ^{13}C nmr chemical shift values observed for the chloro analogue, 2-MeC(O)C₆H₄HgCl, in both d₆-acetone^[13] and CDCl_3 (data obtained by addition of an authentic sample of the chloro analogue to the iodo one).

5.4.1.2 Discussion

Formation of 2-MeC(O)C₆H₄HgI, as determined by its mass spectrum, ^1H nmr spectrum, ^{13}C nmr spectrum and elemental analysis, from the reaction of 2-MeC(O)C₆H₄HgCl with KI was unexpected, with the symmetrisation product [2-MeC(O)C₆H₄]₂Hg being the expected product. The greater solubility of this species over the chloro analogue allowed for

Table 5.4 Comparison of the ^{13}C nmr chemical shifts for compounds of type $2\text{-MeC(O)C}_6\text{H}_4\text{HgX}$ in ppm.

$\text{X} = \text{I}^{\text{a}}$	$\text{X} = \text{Cl}^{\text{a}}$	$\text{X} = \text{Cl}^{\text{b}}$	Assignment	
27.1	29.0	^c	C(8)	
128.7	127.2	128.7	C(n)	
131.5	131.2	131.7	C(n)	
134.3	132.9	133.9	C(n)	
137.3	139.2	138.3	C(n)	
141.2	^d	141.2	C(2)	
159.4	^d	150.0	C(1)	
201.1	^d	201.1	C(7)	

^aMeasured in CDCl_3 . ^bMeasured in d_6 -acetone and taken from Ref. 13.
^cObscured by d_6 -acetone septet. ^dSample too weak to observe.

its use in transmetallation reactions in less polar solvents such as Et_2O , in which the R_2Hg species would normally be used.

5.4.2 Reaction of η^2 -(2-acetylphenyl)tetracarbonylmanganese with Me_3SnCl

A solution of $2\text{-MeC(O)C}_6\text{H}_4\text{Mn(CO)}_4$ (0.154 g, 0.54 mmol) in $30\text{-}40^\circ$ petroleum spirit (20 ml) was added to Me_3SnCl (0.109 g, 0.54 mmol) and refluxed for 18 hours. Infrared analysis of the reaction mixture in the $\nu(\text{CO})$ region indicated no reaction at this stage. The solvent was removed and $40\text{-}60^\circ$ petroleum spirit (15 ml) was added, and the resulting solution refluxed for 23 hours, again monitoring by infrared spectroscopy there was no apparent reaction. Solvent was removed and $60\text{-}80^\circ$ petroleum spirit (15 ml) added. Refluxing for 24 hours lead to no reaction.

5.4.3 Reaction of (2-acetylphenyl)iodomercury(II) with Ph_3SnCl

$2\text{-MeC(O)C}_6\text{H}_4\text{HgI}$ (0.090 g, 0.20 mmol) and Ph_3SnCl (0.079 g, 0.20 mmol) were stirred in Et_2O (10 ml) for 24 hours. The solvent was removed and benzene (15 ml) was added. The solution was refluxed for

48 hours to give a pale yellow solution, which was evaporated to dryness to give a pale yellow solid (0.166 g). This solid was a mixture of the two starting materials, as shown by its ^{13}C nmr spectrum (CDCl_3) (δ 137.4 d, 134.2 d, 131.5 d, 128.7 d and 26.8 q) and its ^{119}Sn nmr spectrum ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$) (δ -50.1 $w_2^{1/2}$ 10 Hz).

5.4.4 Reaction of (2-acetylphenyl)iodomercury(II) with Ph_3SnCl_2

A solution of 2-MeC(O) $\text{C}_6\text{H}_4\text{HgI}$ (0.124 g, 0.35 mmol) and Ph_3SnCl (0.132 g, 0.35 mmol) in CHCl_3 (10 ml) was refluxed for 48 hours. The volume reduced to 2 ml and filtered by gravity. The filtrate was evaporated to dryness to leave a brown-yellow paste (0.097 g) which was a mixture of two compounds: the first was an unknown, with ^{13}C nmr spectrum (CDCl_3) (δ 200.7 s, 148.3 s, 137.7 d, 137.3 d, 134.3 d, 129.8 d and 27.1 q) and the second was tentatively identified as 2-MeC($\overline{\text{O}}$) $\text{C}_6\text{H}_4\text{SnPh}_2\text{Cl}$ by ^{13}C nmr spectroscopy (δ 202.6 s, 140.5 s, 136.6 s, 136.2 d, 136.1 d, 135.4 s, 133.2 d, 131.6 d, 131.1 d, 129.5 d, 129.1 d and 24.3 q) (see Section 5.4.4.1) and by ^{119}Sn nmr spectroscopy (CDCl_3) (δ -195.5 $w_2^{1/2}$ 100 Hz) (see Section 5.4.9).

5.4.4.1 ^{13}C nmr spectroscopy of η^2 -(2-acetylphenyl)chlorodiphenyltin(IV)

The ^{13}C nmr spectrum of η^2 -(2-acetylphenyl)chlorodiphenyltin is consistent with its formulation, with the acetyl carbon resonances at δ 202.6 s and 24.3 q. The six aryl carbon signals associated with the 1,2-disubstituted benzene ring can tentatively be assigned as shown in Table 5.5 as can the four aryl carbon signals from the two equivalent phenyl groups shown in Table 5.6.

The remaining ^{13}C resonances (δ 200.7 s, 148.3 s, 137.7 d, 137.3 d, 134.3 d, 129.8 d and 27.1 q) are, with the exception of one missing singlet aryl carbon signal, consistent with a disubstituted benzene ring, a carbonyl group and a methyl next to a carbonyl group, while the low field signal at δ 148.3 is in the region expected for an aryl carbon bonded to a mercury functionality. This appears initially as if it may be the unreacted

<i>Table 5.5</i> ^{13}C Nmr chemical shifts calculated for the C_6H_4 ring of $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{SnPh}_2\text{Cl}$						
Group	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
δ_{benzene}	128.5	128.5	128.5	128.5	128.5	128.5
$Z_{\text{SnPh}_2\text{Cl}}$	9.0(z1)	7.5(z0)	0.7(zm)	2.0(zp)	0.7(zm)	7.5(z0)
Z_{COMe}	-0.2(z0)	8.5(z1)	-0.2(z0)	-0.4(zm)	4.3(zp)	-0.4(zm)
Calc.	137.3	144.5	129.0	130.1	133.5	135.6
Observed	135.4	140.5	131.1	131.6	133.1	136.2

mercury halide, however this is clearly not the case by comparison with its spectrum shown in Table 5.4. Another, more likely, possibility is that it is the diaryl mercury compound bis(2-acetylphenyl)mercury(II) formed from the symmetrisation of the starting aryl-mercury halide.

<i>Table 5.6</i> ^{13}C Nmr chemical shifts calculated for the phenyl rings of $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{SnPh}_2\text{Cl}$				
Group	C(1)	C(2)	C(3)	C(4)
δ_{benzene}	128.5	128.5	128.5	128.5
$Z_{\text{Sn}^{[56]}(\text{Ph})(\text{Az})\text{Cl}}$	14.1(z1)	7.3(z0)	0.3(zm)	1.0(zp)
Calc.	142.6	135.8	129.8	129.5
Observed	136.6	136.1	129.5	129.1

5.4.5 Reaction of $\eta^2\text{-(2-acetylphenyl)chloromercury(II)}$ with Bu^nSnCl_3

A mixture of $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{HgCl}$ (0.356 g, 1.0 mmol) and Bu^nSnCl_3 (0.590 g, 2.0 mmol) in Et_2O (20 ml) was stirred at room temperature for 24 hours and then refluxed for a further 24 hours. The solvent was removed and the resulting mixture heated at 75°C for 24 hours. Excess Bu^nSnCl_3 was then removed by evaporation at 65°C to give a white solid tentatively identified as $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{SnBu}^n\text{Cl}_2$ (0.278 g, 76 %) by ^1H nmr spectroscopy (d_6 -acetone) (δ 8.37 *d* 1H, 7.88 *d* 1H, 7.79 *dd* 1H, 7.60 *dd* 1H, 1.41 *m* 4H and 0.98 *t* 3H); by ^{13}C nmr spectroscopy (d_6 -acetone) (δ 143.0 *d*, 138.8 *d*, 136.6 *d*, 133.7 *d*, 39.3 *t*, 31.6 *t*, 27.3 *t* and 18.6 *q*); by ^{119}Sn nmr spectroscopy (d_6 -acetone) (δ -299.2 w_2^1 81 Hz) (see

Section 5.4.9) and by solid infrared spectroscopy (major peaks at 1640 s, 1286 s, 772 s, 616 s and 454 s) cm^{-1} . The reaction was also attempted in refluxing *m*-xylene, giving essentially the same results but with poorer yields.

The solid infrared spectrum of the product in the 2000-400 cm^{-1} region as a KBr disc had five major bands at 1640, 1286, 772, 616 and 454 cm^{-1} . This can be compared to the spectrum of 2-MeC(O)C₆H₄HgCl in the same region (1657, 1259, 768 and 601 cm^{-1}). The shift of $\sim 20 \text{ cm}^{-1}$ to lower energy of the $\nu(\text{C}=\text{O})$ band for the product suggests a decrease in the C-O bond. The 454 cm^{-1} band evident in the tin derivative, but absent in the mercury can be assigned to the $\nu(\text{Sn-Cl})$ stretch.

5.4.5.1 ¹H and ¹³C nmr spectroscopy of η^2 -(2-acetylphenyl)butyldichlorotin(IV)

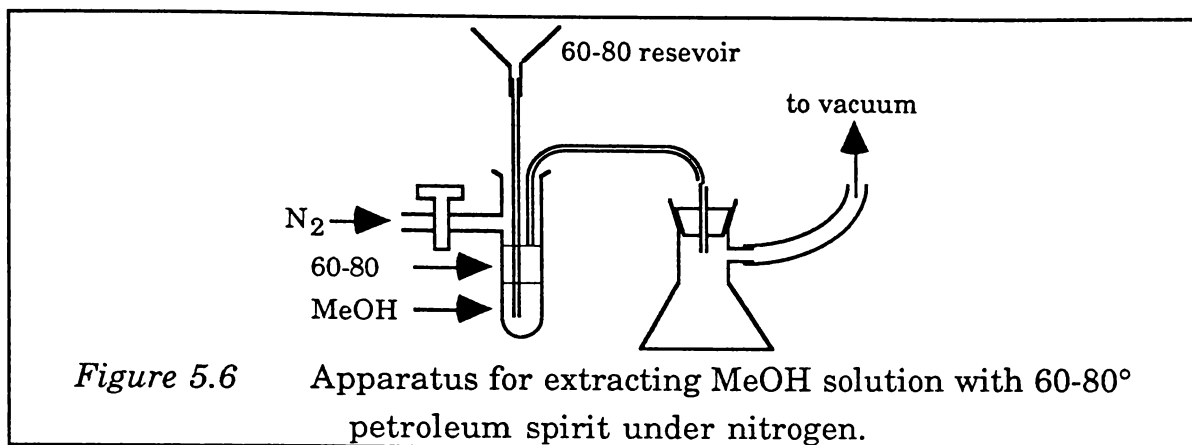
The ¹H nmr spectrum of the product in d₆-acetone can be divided into two sections; the bands associated with the aryl function and the bands related to the butyl group. In the aryl region four bands are observed at δ 8.37 *d*, 7.88 *d*, 7.79 *dd* and 7.60 *dd*, with the two *dd* appearing as triplets due to indistinguishable ³J couplings to two neighbouring, chemically different protons. This is the expected pattern for the proton signals of a 1,2-disubstituted benzene ring. The two doublet protons, H(3) and H(6), resonate at lowest field. This finding is in accord with the recorded ¹H nmr spectra of several *ortho*-manganated acetophenones^[57] and several *ortho*-stannated thiobenzophenones.^[58] Only two of the expected four signals were observed for the n-butyl group (δ 1.41 *m* 4H and 0.98 *t* 3H). The three proton triplet at δ 0.98 can be assigned to the methyl protons and the four proton multiplet at δ 1.41 to the methylene protons on C(2) and C(3). The broadness of the base of the d₆-acetone septet at δ 2.17 suggests that the remaining methylene proton resonances are obscured. These can be compared to the corresponding resonances for the n-butyl

protons for Bu^nSnCl_3 (d_6 -acetone) (δ 2.69 t 2H, 2.05 m 2H, 1.62 m 2H and 1.10 t 3H).

As for the ^1H nmr spectrum the ^{13}C nmr spectrum of the product in d_6 -acetone can be divided into the aryl and alkyl regions. Four signals (δ 143.0 d, 138.8 d, 136.6 d and 133.7 d) were observed in the aryl region as would be expected for a 1,2-disubstituted benzene ring. The four carbon resonances expected for the n-butyl fragment of the molecule were observed at δ 39.3 t, 31.6 t, 27.3 t and 18.6 q. These are in good agreement with the ^{13}C resonances found for Bu^nSnCl_3 (δ 41.7 t, 31.7 t, 29.8 t and 18.0 q). The singlet carbons were not observed due to the low solubility of the product and the methyl carbon attached to the carbonyl was obscured by the d_6 -acetone methyl resonance.

5.4.6 Reaction of η^2 -(2-acetylphenyl)tetracarbonylmanganese with SnCl_2

A solution of $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\overline{\text{Mn}}(\text{CO})_4$ (0.127 g, 0.44 mmol) and SnCl_2 (0.168 g, 0.89 mmol) in methanol (10 ml) was refluxed under N_2 for 2 hours. After this time most of the $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\overline{\text{Mn}}(\text{CO})_4$ had reacted as evident by infrared spectroscopy. The MeOH solution was extracted (see Figure 5.6) with 60-80° petroleum spirit until the washings were colourless. The washings contained $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\overline{\text{Mn}}(\text{CO})_4$ and $\text{Mn}_2(\text{CO})_{10}$ as identified by infrared spectroscopy $\nu(\text{CO})_{\text{hexane}}$ (2083 m, 1995 vs and 1947 s) cm^{-1} and $\nu(\text{CO})_{\text{hexane}}$ (2046 s, 2015 vs and 1984 s) cm^{-1} respectively. The MeOH was then removed to leave a pale-yellow residue, from which small amount of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ was isolated as identified by a full X-ray crystal structure determination (see Appendix 8). The remaining white residue, which had no resonances in its ^{13}C nmr spectrum, remains uncharacterised.



5.4.7 Reaction of (2-acetylphenyl)chloromercury(II) with SnCl_2

A suspension of 2-MeC(O)C₆H₄HgCl (0.245 g, 0.69 mmol) and anhydrous SnCl_2 (0.131 g, 0.69 mmol) in *m*-xylene was refluxed for 96 hours to give a brown-yellow solution. The volume was reduced to ~1 ml and 60-80° petroleum spirit (10 ml) was added. The resulting clear solution was decanted off and the residue extracted with CH_2Cl_2 and filtered on a Buchner to give a yellow-brown solid (0.123 g), tentatively identified as 2-MeC($\overline{\text{O}}$)C₆H₄SnCl₃ (52 %) by a partial X-ray crystal structure analysis (see Section 5.4.7.2); by ^1H nmr spectroscopy (d_6 -acetone/ CDCl_3) (δ 8.46 *d* 1H, 8.27-7.77 *m* 3H and 3.07 *s* 3H); by ^{13}C nmr spectroscopy (d_6 -acetone/ CDCl_3) (δ 204.1 *s*, 144.5 *s*, 137.4 *d*, 134.4 *s*, 134.2 *d*, 132.5 *d*, 131.6 *d* and 24.3 *q*) and by ^{119}Sn nmr spectroscopy (d_6 -acetone/ CDCl_3) (RT δ -199.4 $w_2^{1/2}$ 40 Hz; -40°C δ -204.7 $w_2^{1/2}$ 17 Hz) (see Section 5.4.9).

5.4.7.1 ^1H and ^{13}C nmr spectroscopy of η^2 -(2-acetylphenyl)trichlorotin(IV)

The ^1H nmr spectrum of the product in d_6 -acetone/ CDCl_3 is consistent with the spectrum expected for a disubstituted benzene ring and a methyl ketone. In the aryl region four proton resonances are observed: a one proton doublet at δ 8.46 and a three proton unresolved

multiplet ranging from δ 8.27 to 7.77. The three proton singlet at δ 3.07 can be assigned to the methyl protons of the methyl ketone fragment.

The familiar pattern, recorded in d_6 -acetone/ $CDCl_3$, observed for the ^{13}C nmr spectrum of *ortho*-metallated acetophenones is also observed for $2-MeC(\overline{O})C_6H_4\overline{SnCl_3}$. The carbonyl carbon resonance was observed at δ 204.1, the two substituted aryl carbon atom resonances at 144.5 and 134.4, the remaining four unsubstituted aryl carbon atom resonances at 137.4 d, 134.2 d, 132.5 d and 131.6 d, and the quartet associated with the methyl carbon observed at 24.3.

5.4.7.2 Attempted X-ray structure determination of η^2 -(2-acetylphenyl)trichlorotin(IV)

Pale-yellow crystals of $2-MeC(\overline{O})C_6H_4\overline{SnCl_3}$ were grown from a solution in $CDCl_3$ which was allowed to evaporate at room temperature.

One of the well-formed crystals was attached to a fine glass fibre with grease and mounted on a goniometer. Preliminary precession photography indicated a space group of $P2_1/n$ with $a = 12.1$, $b = 13.6$ and $c = 8.4 \text{ \AA}$, $\beta = 90.3^\circ$, $U = 1387 \text{ \AA}^3$ and $z = 4$. Crystals sent for intensity data collection were amorphous on arrival as were the remaining ones on examination for further crystals. All attempts to grow further crystals failed.

A sensible density for a compound of the type $RSnCl_3$ of 1.7 g cm^{-3} is in accord with the calculated ρ of 1.65 g cm^{-3} for the above unit cell with four molecules of $2-MeC(\overline{O})C_6H_4\overline{SnCl_3}$ per unit cell.

5.4.8 Reaction of (2-benzoylphenyl)chloromercury(II) with $SnCl_2$

The reaction was performed as for $2-MeC(O)C_6H_4HgCl$ with $SnCl_2$ using $2-PhC(O)C_6H_4HgCl$ (0.07 g, 0.2 mmol), $SnCl_2$ (0.038 g, 0.2 mmol) and *m*-xylene (5 ml) with the following modifications. The reflux period

was 48 hours. The precipitate was washed with 30-40° petroleum spirit (40 ml) and CH_2Cl_2 (50 ml) and the residue extracted with dry acetone (30 ml) leaving a metallic residue. Evaporation of the acetone gave a small amount of a yellow-brown residue with an ^{119}Sn nmr spectrum in d_6 -acetone/acetone (δ -120.0 w_2^1 800 Hz).

With the small quantity of product meaningful ^{13}C nmr data were not obtainable.

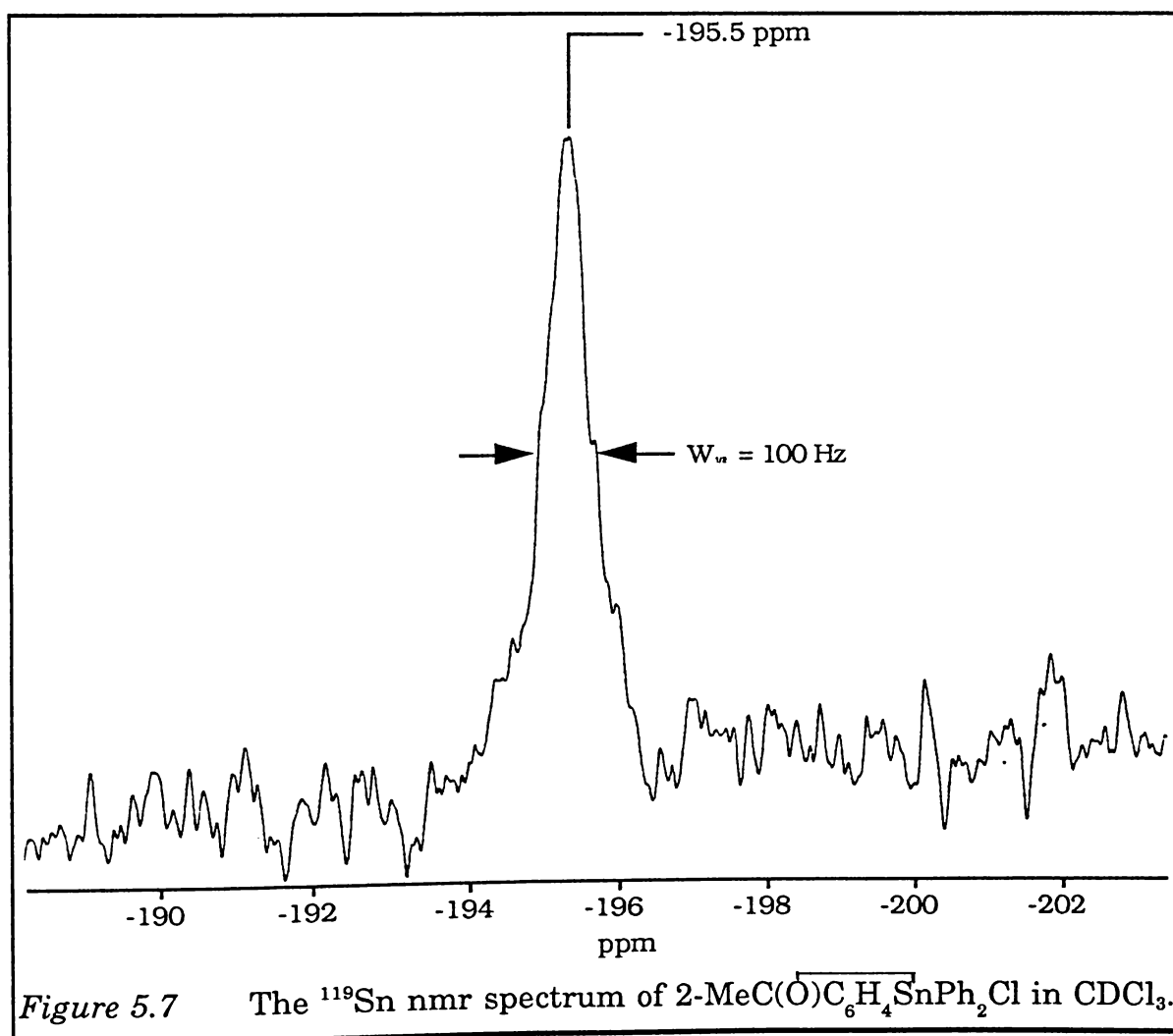
5.4.9 ^{119}Sn Nmr Spectroscopy of the Aryl-Tin Derivatives

The ^{119}Sn nmr spectra of the aryl-tin species prepared in this work are summarised in Table 5.7, with a representative spectrum shown in Figure 5.7.

Table 5.7 Comparison of the ^{119}Sn nmr spectra for the aryl-tin species prepared in this work.			
Compound	Solvent	δ (ppm)	w_2^1 (Hz)
$2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{SnPh}_2\text{Cl}$	CDCl_3	-195.5	100
$2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{SnCl}_3$	d_6 -acetone/ CDCl_3 , RT	-199.4	40
	-40°C	-204.7	17
$2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{SnBu}^n\text{Cl}_2$	d_6 -acetone	-299.2	81
$2\text{-PhC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{SnCl}_3$	d_6 -acetone/acetone	-120.0	800

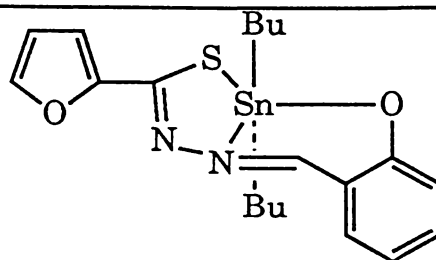
Studies of the ^{119}Sn nmr spectra of organo-tin species in comparison with the coordination number of tin in the species have been performed. While resonances varied over large ranges depending on the geometry of the attached groups,^[59] it was found that the larger the coordination number of the tin species the further upfield the signals were observed.^[60,61] The ^{119}Sn chemical shift range for four-coordinate compounds was δ +200 to -60, for five-coordinate δ -90 to -190 and for six-coordinate δ -210 to -400.

In accord with this all but one of the complexes show only one signal in the range δ -120.0 to -199.4 ppm, suggesting five-coordinate tin. The one anomalous complex, 2-MeC($\overline{\text{O}}$)C₆H₄SnBuⁿCl₂, has a single ¹¹⁹Sn resonance at δ -299.2 suggesting a six-coordinate species (the five coordinate butyl complex Bu₂SnL, LH₂ = salicylaldehyde-2-furancarboxy-hydrazone as shown in Figure 5.8, has a tin resonance at δ -134.8 ppm^[61]). Six-coordination is not precluded by the other spectroscopic evidence; ¹H and ¹³C nmr spectroscopy indicated the presence of one *ortho*-substituted acetophenone while meaningful results from the integration of the ¹H nmr spectrum were precluded by peak overlaps with Et₂O and d₆-acetone. If RHgX was to react with BuⁿSnCl₃ in a 2:1 ratio then, with oxygen coordination by both acetophenone groups, six-coordination is feasible if



the two R groups are chemically equivalent.

Figure 5.8 Suggested structure of Bu_2SnL , $\text{LH}_2 = \text{salicylaldehyde-2-furan-carboxyhydrazone}$.



5.4.10 Discussion

The attempted transmetallation reactions using the *ortho*-metallated aryl ketone $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$ with Me_3SnCl or with SnCl_2 were unsuccessful. However, previous success with aryl transfer from arylmercury complexes to tin, as discussed at the beginning of Section 5.4, suggested that this may be a more successful method for the production of aryltin species. The desired *ortho*-mercured aryl ketones are easily prepared as described in Section 1.4.5 from the analogous *ortho*-manganated aryl ketone. Both the redox transmetallation reactions between SnCl_2 and $2\text{-RC}(\text{O})\text{C}_6\text{H}_4\text{HgCl}$ ($\text{R} = \text{Ph}, \text{Me}$) and the transmetallation reactions between $\text{R}_n\text{SnCl}_{4-n}$ ($\text{R} = \text{Bu}^n, n = 1; \text{R} = \text{Ph}, n = 2$) and $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{HgX}$ afforded aryltin complexes. The reaction between Ph_3SnCl and $2\text{-MeC}(\text{O})\text{C}_6\text{H}_4\text{HgI}$ did not lead to any aryltin products. This difference in reactivity between the di- and tri-phenyltin(IV) chlorides may be due to the more acidic character of the former, which could facilitate the formation of an aryl bridge between both metals in the transfer of the aryl group. A similar difference in reactivity was observed in the reaction

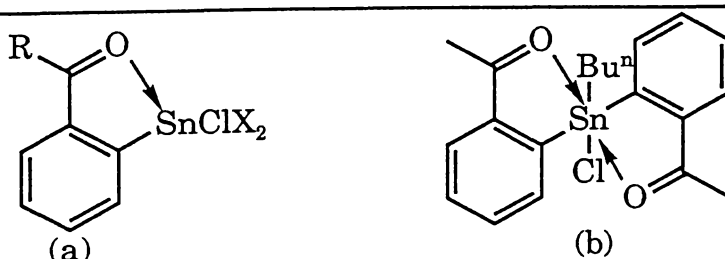


Figure 5.9 Proposed structures for the products from the mercury to tin transmetallations (a) $2\text{-RC}(\text{O})\text{C}_6\text{H}_4\text{SnX}_2\text{Cl}$ ($\text{R} = \text{Ph}, \text{X} = \text{Cl}; \text{R} = \text{Me}, \text{X} = \text{Cl}, \text{Ph}$) and (b) $[2\text{-MeC}(\text{O})\text{C}_6\text{H}_4]_2\text{Sn}(\text{Bu}^n)\text{Cl}$.

of phenyltin(IV) chlorides with 2-PhN=NC₆H₄HgCl in the presence of Me₄NCl. In this case transmetallation was observed in the monophenyl case^[52] but not in the diphenyl one.^[54]

The aryltin halide complexes prepared above were characterised by spectroscopic means. The products formed were assumed to be chlorides. However, in the cases where arylmercury iodides were used as transmetallation reagents, there was no evidence to preclude iodide from the products. ¹¹⁹Sn nmr spectroscopy of the products from the redox transmetallations and the reaction with Ph₂SnCl₂ supports their formulation as the five-coordinate tin(IV) complexes 2-RC($\overline{\text{O}}$)C₆H₄Sn(Ph)_nCl_{3-n} (R = Me, n = 0 or 2; R = Ph, n = 0) (see Figure 5.9). This suggests that the oxygen atom on the *ortho*-carbonyl function is bonding to the tin atom, to some extent. The high field ¹¹⁹Sn resonance of the product from the reaction of BuⁿSnCl₃ with 2-MeC(O)C₆H₄HgCl suggests a six-coordinate tin species. Six-coordination would probably arise from the transfer of two aryl ketone functions onto the tin atom with displacement of two chloride groups to give a complex of the type [2-MeC($\overline{\text{O}}$)C₆H₄]₂Sn(Buⁿ)Cl shown in Figure 5.9. The ¹³C and ¹H nmr spectra of all of the tin complexes are consistent with 1,2-disubstituted -C($\overline{\text{O}}$)C₆H₄- functionality.

Support to these formulations is given by the results of Jousseume *et al.*^[62] who reported the structure of 2-MeOC($\overline{\text{O}}$)C₆H₄SnMe₃, which was prepared by a similar route. The tin-oxygen distance in the solid state was 278.1 pm, which falls within the range of previously reported tin-oxygen compounds.^[63]

Triaryltin halides are usually obtained by dearylation reactions of tetraaryltin species with X₂ or HX, or by transmetallation reactions with aryl derivatives of Li, Mg, Al or Sn. In the majority of these cases

homo-aryltin(IV) complexes are formed. Of the few hetero-aryltin(IV) complexes like $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Sn}(\text{Ph})_2\text{Cl}$, formation was by transmetallation reactions between phenyltin halides and arylcopper^[64] or arylmercury^[54] compounds.

It is apparent from the above results that *ortho*-stannated aryl ketones are accessible by this route, but that a more detailed study is required to fully establish their chemistry.

5.5 CONCLUSION

It is evident from all of the above results that successful aryl transfer reactions from *ortho*-manganated aryl ketones to mercury, cannot be extended straightforwardly to tin, aluminium or phosphorus halides. Manganese-aryl-carbon bond cleavage does occur as is shown by the formation of the complexes $[\text{Mn}(\text{CO})_4\text{Cl}]_2$ and $\text{Mn}_2(\text{CO})_{10}$ from the reaction of $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$ with SnCl_2 or AlCl_3 respectively, but no aryl-tin or aryl-aluminium species could be characterised. Manganese-aryl-carbon bond cleavage was also observed in the formation of $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ from the reaction of Ph_2PCl with $2\text{-MeC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$, where initially carbonyl substitution on the $\text{Mn}(\text{CO})_4$ group was observed, followed by loss of the acetophenone derivative with dimerisation of the manganese fragment.

While acylaryltin complexes were not directly formed from reaction with $2\text{-RC}(\overline{\text{O}})\text{C}_6\text{H}_4\text{Mn}(\text{CO})_4$, they could be formed via the intermediate mercury derivative formed by a transmetallation reaction from manganese to mercury. Reaction of these arylmercury complexes with tin halides afforded five- and six-coordinate tin halide derivatives incorporating keto-aryl units, but more work is needed to establish the optimum conditions for specific examples.

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Appendices

APPENDIX ONE

ISOTOPE PATTERN CALCULATOR, A PROGRAM TO CALCULATE ISOTOPIC RATIOS FOR MOLECULAR FRAGMENTS.

Isotope Pattern Calculator calculates the expected isotope ratio for any given molecular fragment. The natural abundances for all the elements,^[1] as well as some common fragments, are incorporated in the package. If you ever tried to calculate the isotope pattern for $\text{As}_2\text{Fe}_6(\text{CO})_{22-n}$ fragments, or the like, by hand then you will understand the reasons behind the development of this program.

What Isotope Pattern Calculator (v.1.6.1) Does

Isotope Pattern Calculator can be used to calculate the isotopic ratio for any molecular fragment. The pattern can be either displayed on the screen, printed, or saved to disk to be read into a graphics package or word processor. Up to eight patterns are maintained in memory and can be printed on one page.

To calculate isotopic ratios the formula of the fragment is typed into the molecular formula box (see Figure A1.1). Various formats such as $\text{Ge}(\text{SnMe}_3)_4$ and $[\text{FeCp}(\text{CO})_2]_2$ are accepted. Then the mouse is used to click the "Calculate" button. The percentage isotopic ratio is shown in the main window.^[2] To view the ratio graphically the "Display" button is selected to provide the display window as shown in Figure A1.2. The isotopic ratios of the last eight fragments calculated can be cycled through

using the previous and next buttons. The format and font menus can be used to change the appearance of the plot which can then be printed.

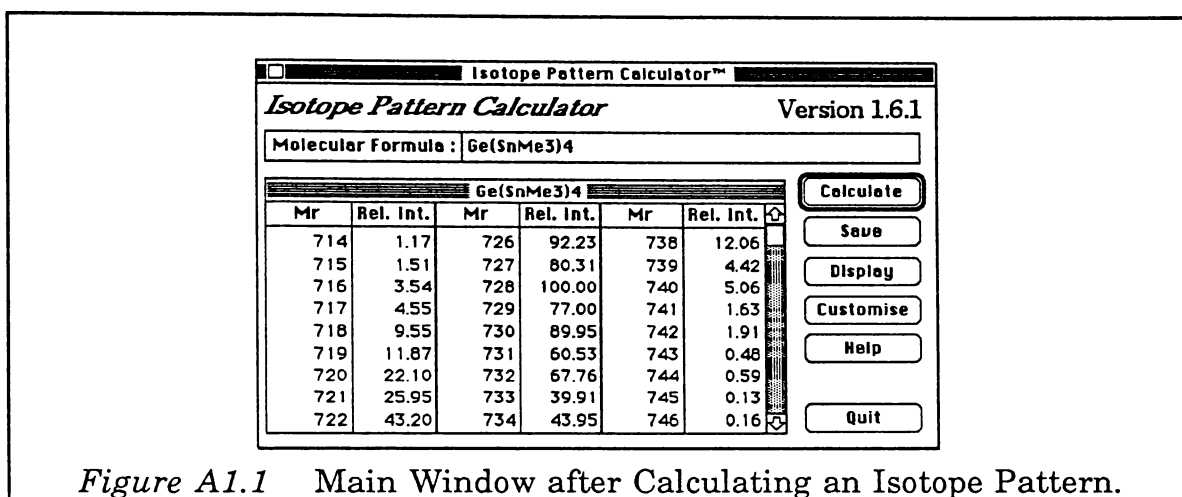


Figure A1.1 Main Window after Calculating an Isotope Pattern.

The “Customise” function allows the entering of abundance data for isotopically enriched species and commonly used groups into a library file.

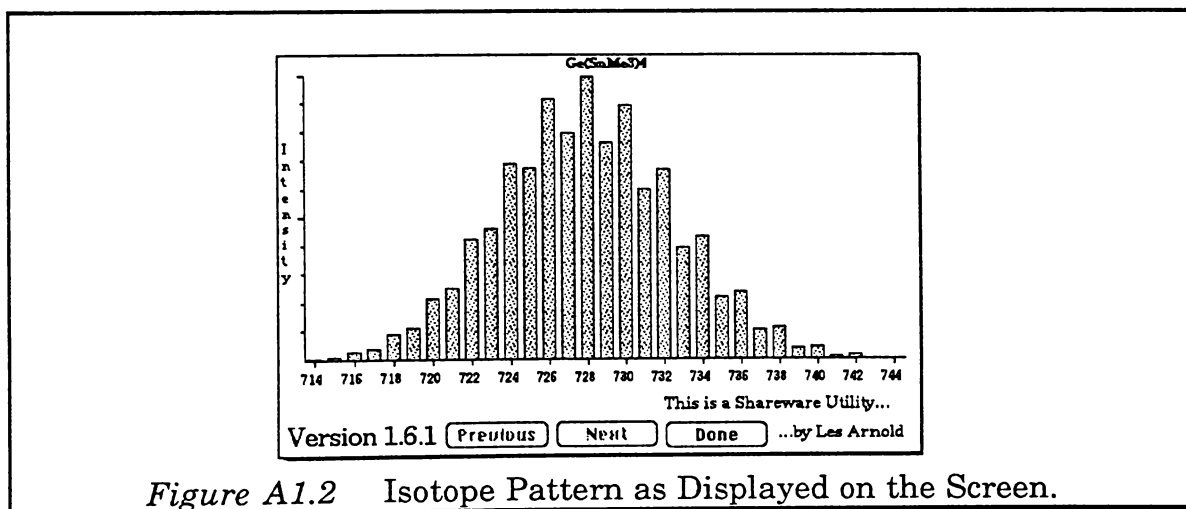


Figure A1.2 Isotope Pattern as Displayed on the Screen.

Selecting “Print Pattern...” from the file menu will bring up the print window, where the eight most recently calculated isotope patterns can be manipulated and then printed.

If there are any problems with the operation of Isotope Pattern Calculator there is on line help available by clicking the mouse in the “Help” button on the main window.

Miscellaneous Information

Isotope Pattern Calculator (v.1.6.1) was written entirely in THINK Pascal and hence some parts are © THINK Technologies Inc. This utility is compatible with all models of Apple Macintosh on which it has been tested^[3] and with system versions 4.2 and later. It is distributed under the share-ware system. A copy of Isotope Pattern Calculator can be obtained by writing to the author. We do request that a disk be sent on which to copy the program.

1. Elemental abundances were taken from "CRC Handbook of Chemistry and Physics," 64th Edition, R. C. Weast Ed., (1983-4).
2. Isotopic percentages are accurate to within $\pm 0.005\%$.
3. The models tested on include the : 512 Enhanced, Plus, SE, Classic and the IIfx.

APPENDIX TWO

POSITIONAL, THERMAL AND BOND LENGTH DATA FOR [Fe₂(CO)₈(μ₄-As)]₂[Fe₂(CO)₆]

Table A2.1 Bond lengths for [Fe₂(CO)₈(μ₄-As)]₂[Fe₂(CO)₆] (pm).

As(1)---Fe(1)	235(1)	Fe(4)---C(44)	174(6)
As(1)---Fe(2)	233.9(9)	Fe(5)---Fe(6)	272(1)
As(1)---Fe(3)	242(1)	Fe(5)---C(51)	179(6)
As(1)---Fe(4)	240.8(9)	Fe(5)---C(52)	175(9)
As(2)---Fe(1)	233(1)	Fe(5)---C(53)	16(1)
As(2)---Fe(2)	235(1)	Fe(5)---C(54)	178(7)
As(2)---Fe(5)	241(1)	Fe(6)---C(61)	184(7)
As(2)---Fe(6)	239(1)	Fe(6)---C(62)	184(6)
Fe(1)---Fe(2)	268(1)	Fe(6)---C(63)	177(8)
Fe(1)---C(11)	177(6)	Fe(6)---C(64)	179(6)
Fe(1)---C(12)	175(6)	C(11)---O(11)	114(6)
Fe(1)---C(13)	184(5)	C(21)---O(21)	118(6)
Fe(2)---C(21)	175(6)	C(22)---O(22)	114(6)
Fe(2)---C(22)	178(6)	C(31)---O(31)	115(7)
Fe(2)---C(23)	178(5)	C(32)---O(32)	121(6)
Fe(3)---Fe(4)	275(1)	C(41)---O(41)	109(6)
Fe(3)---C(31)	170(7)	C(42)---O(42)	112(6)
Fe(3)---C(32)	176(5)	C(43)---O(43)	115(6)
Fe(3)---C(33)	161(6)	C(51)---O(51)	116(6)
Fe(3)---C(34)	170(7)	C(54)---O(54)	111(7)
Fe(4)---C(41)	187(6)	C(61)---O(61)	116(7)
Fe(4)---C(42)	175(6)	C(63)---O(63)	125(7)
Fe(4)---C(43)	182(5)		

Table A2.2 Bond angles for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$ (°).

Fe(1)-As(1)-Fe(2)	69.9(3)	As(1)-Fe(4)-Fe(3)	55.4(3)
Fe(1)-As(1)-Fe(3)	140.2(4)	As(1)-Fe(4)-C(41)	88(2)
Fe(1)-As(1)-Fe(4)	126.0(4)	As(1)-Fe(4)-C(42)	101(2)
Fe(2)-As(1)-Fe(3)	133.3(4)	As(1)-Fe(4)-C(43)	156(2)
Fe(2)-As(1)-Fe(4)	129.0(4)	As(1)-Fe(4)-C(44)	88(2)
Fe(3)-As(1)-Fe(4)	69.5(3)	Fe(3)-Fe(4)-C(41)	87(2)
Fe(1)-As(2)-Fe(2)	70.0(3)	Fe(3)-Fe(4)-C(42)	156(2)
Fe(1)-As(2)-Fe(5)	128.5(4)	Fe(3)-Fe(4)-C(43)	100(2)
Fe(1)-As(2)-Fe(6)	132.7(4)	Fe(3)-Fe(4)-C(44)	90(2)
Fe(2)-As(2)-Fe(5)	127.9(4)	C(41)-Fe(4)-C(42)	91(3)
Fe(2)-As(2)-Fe(6)	139.8(4)	C(41)-Fe(4)-C(43)	88(3)
Fe(5)-As(2)-Fe(6)	69.2(3)	C(41)-Fe(4)-C(44)	176(3)
As(1)-Fe(1)-As(2)	84.4(3)	C(42)-Fe(4)-C(43)	102(3)
As(1)-Fe(1)-Fe(2)	54.9(3)	C(42)-Fe(4)-C(44)	89(3)
As(1)-Fe(1)-C(11)	105(2)	C(43)-Fe(4)-C(44)	94(3)
As(1)-Fe(1)-C(12)	92(2)	As(2)-Fe(5)-Fe(6)	55.2(3)
As(1)-Fe(1)-C(13)	149(2)	As(2)-Fe(5)-C(51)	88(2)
As(2)-Fe(1)-Fe(2)	55.4(3)	As(2)-Fe(5)-C(52)	84(3)
As(2)-Fe(1)-C(11)	93(2)	As(2)-Fe(5)-C(53)	148(4)
As(2)-Fe(1)-C(12)	166(2)	As(2)-Fe(5)-C(54)	109(2)
As(2)-Fe(1)-C(13)	87(2)	Fe(6)-Fe(5)-C(51)	84(2)
Fe(2)-Fe(1)-C(11)	141(2)	Fe(6)-Fe(5)-C(52)	89(3)
Fe(2)-Fe(1)-C(12)	112(2)	Fe(6)-Fe(5)-C(53)	94(4)
Fe(2)-Fe(1)-C(13)	96(2)	Fe(6)-Fe(5)-C(54)	163(2)
C(11)-Fe(1)-C(12)	100(3)	C(51)-Fe(5)-C(52)	172(3)
C(11)-Fe(1)-C(13)	104(3)	C(51)-Fe(5)-C(53)	84(4)
C(12)-Fe(1)-C(13)	88(3)	C(51)-Fe(5)-C(54)	90(3)
As(1)-Fe(2)-As(2)	84.1(3)	C(52)-Fe(5)-C(53)	100(5)
As(1)-Fe(2)-Fe(1)	55.2(3)	C(52)-Fe(5)-C(54)	94(3)
As(1)-Fe(2)-C(21)	158(2)	C(53)-Fe(5)-C(54)	101(5)
As(1)-Fe(2)-C(22)	101(2)	As(2)-Fe(6)-Fe(5)	55.6(3)
As(1)-Fe(2)-C(23)	89(2)	As(2)-Fe(6)-C(61)	95(2)
As(2)-Fe(2)-Fe(1)	54.6(3)	As(2)-Fe(6)-C(62)	152(2)
As(2)-Fe(2)-C(21)	86(2)	As(2)-Fe(6)-C(63)	81(2)
As(2)-Fe(2)-C(22)	104(2)	As(2)-Fe(6)-C(64)	96(2)
As(2)-Fe(2)-C(23)	150(2)	Fe(5)-Fe(6)-C(61)	79(2)
Fe(1)-Fe(2)-C(21)	103(2)	Fe(5)-Fe(6)-C(62)	98(2)
Fe(1)-Fe(2)-C(22)	147(2)	Fe(5)-Fe(6)-C(63)	100(2)
Fe(1)-Fe(2)-C(23)	98(2)	Fe(5)-Fe(6)-C(64)	147(2)
C(21)-Fe(2)-C(22)	99(3)	C(61)-Fe(6)-C(62)	88(3)
C(21)-Fe(2)-C(23)	89(2)	C(61)-Fe(6)-C(63)	177(3)
C(22)-Fe(2)-C(23)	104(2)	C(61)-Fe(6)-C(64)	87(3)
As(1)-Fe(3)-Fe(4)	55.1(3)	C(62)-Fe(6)-C(63)	94(3)
As(1)-Fe(3)-C(31)	84(2)	C(62)-Fe(6)-C(64)	110(3)
As(1)-Fe(3)-C(32)	145(2)	C(63)-Fe(6)-C(64)	91(3)
As(1)-Fe(3)-C(33)	91(2)	Fe(1)-C(11)-O(11)	177(6)
As(1)-Fe(3)-C(34)	111(2)	Fe(2)-C(21)-O(21)	173(5)
Fe(4)-Fe(3)-C(31)	93(2)	Fe(2)-C(22)-O(22)	171(6)
Fe(4)-Fe(3)-C(32)	90(2)	Fe(3)-C(31)-O(31)	169(6)

.cont ...

Table A2.2 ...continued.

Fe(4)-Fe(3)-C(33)	87(2)	Fe(3)-C(32)-O(32)	177(5)
Fe(4)-Fe(3)-C(34)	164(2)	Fe(4)-C(41)-O(41)	173(6)
C(31)-Fe(3)-C(32)	99(3)	Fe(4)-C(42)-O(42)	175(5)
C(31)-Fe(3)-C(33)	173(3)	Fe(4)-C(43)-O(43)	174(5)
C(31)-Fe(3)-C(34)	92(3)	Fe(5)-C(51)-O(51)	172(6)
C(32)-Fe(3)-C(33)	87(3)	Fe(5)-C(54)-O(54)	177(6)
C(32)-Fe(3)-C(34)	102(3)	Fe(6)-C(61)-O(61)	166(6)
C(33)-Fe(3)-C(34)	85(3)	Fe(6)-C(63)-O(63)	170(6)

Table A2.3 Final positional parameters for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
As(1)	0.1790(2)	0.0822(3)	0.3584(3)	As(2)	0.0602(2)	0.1637(3)	0.3182(3)
Fe(1)	0.0818(3)	0.0401(4)	0.3616(5)	Fe(2)	0.1327(3)	0.1106(4)	0.2325(5)
Fe(3)	0.2486(4)	0.1502(4)	0.4438(5)	Fe(4)	0.2641(3)	0.0047(4)	0.3831(5)
Fe(5)	-0.0326(4)	0.2157(6)	0.2772(6)	Fe(6)	0.0399(4)	0.2791(5)	0.3924(6)
C(11)	0.058(3)	0.057(4)	0.465(4)	O(11)	0.041(2)	0.070(2)	0.530(2)
C(12)	0.103(3)	-0.055(3)	0.370(4)	O(12)	0.383(2)	0.119(3)	0.888(3)
C(13)	0.016(2)	0.008(3)	0.306(3)	O(13)	0.479(2)	0.518(2)	0.730(3)
C(21)	0.079(2)	0.108(3)	0.154(3)	O(21)	0.048(2)	0.106(2)	0.096(2)
C(22)	0.174(3)	0.190(3)	0.197(3)	O(22)	0.206(2)	0.235(3)	0.173(3)
C(23)	0.167(2)	0.030(3)	0.186(3)	O(23)	0.305(1)	0.018(2)	0.655(2)
C(31)	0.206(3)	0.121(4)	0.524(4)	O(31)	0.181(2)	0.109(2)	0.585(2)
C(32)	0.317(2)	0.146(3)	0.494(3)	O(32)	0.363(2)	0.141(3)	0.531(3)
C(33)	0.283(2)	0.180(3)	0.362(4)	O(33)	0.302(2)	0.294(2)	0.790(2)
C(34)	0.229(3)	0.243(4)	0.457(4)	O(34)	0.222(2)	0.190(2)	0.967(3)
C(41)	0.228(3)	-0.031(4)	0.480(4)	O(41)	0.204(2)	-0.055(3)	0.531(3)
C(42)	0.246(3)	-0.079(3)	0.329(3)	O(42)	0.237(2)	-0.133(2)	0.296(2)
C(43)	0.334(2)	-0.019(3)	0.429(3)	O(43)	0.379(2)	-0.029(2)	0.458(3)
C(44)	0.294(3)	0.041(3)	0.292(4)	O(44)	0.318(2)	0.446(2)	0.728(3)
C(51)	0.005(3)	0.275(4)	0.205(4)	O(51)	0.034(2)	0.307(2)	0.157(3)
C(52)	-0.061(4)	0.156(5)	0.354(5)	O(52)	0.418(2)	0.104(3)	0.114(3)
C(53)	-0.079(5)	0.285(7)	0.281(7)	O(53)	0.382(3)	0.333(4)	0.204(3)
C(54)	-0.061(3)	0.161(4)	0.193(4)	O(54)	-0.078(2)	0.125(2)	0.142(3)
C(61)	-0.016(3)	0.237(4)	0.460(4)	O(61)	-0.051(2)	0.224(3)	0.511(3)
C(62)	0.004(3)	0.372(3)	0.403(4)	O(62)	0.486(2)	0.433(2)	0.088(2)
C(63)	0.096(3)	0.315(4)	0.327(4)	O(63)	0.133(2)	0.350(2)	0.285(2)
C(64)	0.091(2)	0.264(3)	0.475(3)	O(64)	0.115(2)	0.246(2)	0.039(3)

Table A2.4 Final thermal parameters for $[\text{Fe}_2(\text{CO})_8(\mu_4\text{-As})]_2[\text{Fe}_2(\text{CO})_6]$

Atom	U11	U22	U33	U23	U13	U12	
As(1)	0.015(3)	0.009(3)	0.016(3)	0.001(3)	-0.002(3)	-0.002(3)	
As(2)	0.018(3)	0.014(3)	0.011(3)	0.007(3)	0.003(3)	0.001(3)	
Fe(1)	0.016(5)	0.017(5)	0.013(4)	0.000(4)	0.004(4)	0.000(4)	
Fe(2)	0.005(4)	0.014(5)	0.026(5)	0.012(4)	-0.005(4)	0.003(4)	
Fe(3)	0.018(4)	0.013(4)	0.015(4)	-0.005(4)	-0.001(4)	-0.004(4)	
Fe(4)	0.012(5)	0.012(4)	0.032(5)	0.009(4)	-0.003(4)	0.006(4)	
Fe(5)	0.018(6)	0.052(7)	0.031(6)	-0.003(5)	0.004(5)	0.010(5)	
Fe(6)	0.016(5)	0.030(6)	0.040(5)	0.002(5)	0.003(5)	-0.003(5)	
Atom	U	Atom	U	Atom	U	Atom	U
C(11)	0.03(2)	O(11)	0.03(1)	C(42)	0.03(1)	O(42)	0.03(1)
C(12)	0.03(2)	O(12)	0.05(1)	C(43)	0.01(1)	O(43)	0.04(1)
C(13)	0.01(1)	O(13)	0.05(1)	C(44)	0.03(2)	O(44)	0.04(1)
C(21)	0.020(0)	O(21)	0.03(1)	C(51)	0.03(2)	O(51)	0.04(1)
C(22)	0.02(1)	O(22)	0.06(1)	C(52)	0.08(3)	O(52)	0.06(2)
C(23)	0.01(1)	O(23)	0.013(0)	C(53)	0.13(4)	O(53)	0.10(2)
C(31)	0.05(2)	O(31)	0.03(1)	C(54)	0.04(2)	O(54)	0.04(1)
C(32)	0.020(0)	O(32)	0.06(1)	C(61)	0.03(2)	O(61)	0.06(1)
C(33)	0.019(0)	O(33)	0.02(1)	C(62)	0.03(2)	O(62)	0.03(1)
C(34)	0.04(2)	O(34)	0.04(1)	C(63)	0.06(2)	O(63)	0.04(1)
C(41)	0.03(2)	O(41)	0.05(1)	C(64)	0.02(1)	O(64)	0.04(1)

APPENDIX THREE

POSITIONAL, THERMAL AND BOND LENGTH DATA FOR $\text{PhP}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}]_2$

Table A3.1 Bond lengths for $\text{PhP}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}]_2$ (pm).

P(1)---C(11)	1.81(1)	C(23)---C(24)	1.39(2)
P(1)---C(21)	1.81(1)	C(24)---C(25)	1.38(2)
P(1)---O(22)	1.792(9)	C(25)---C(26)	1.39(2)
P(1)---C(31)	1.81(1)	C(27)---O(21)	1.23(1)
P(1)---O(32)	1.783(8)	C(27)---O(22)	1.33(2)
C(11)---C(12)	1.41(2)	C(31)---C(32)	1.39(1)
C(11)---C(16)	1.39(2)	C(31)---C(36)	1.39(2)
C(12)---C(13)	1.39(2)	C(32)---C(33)	1.42(2)
C(13)---C(14)	1.38(2)	C(32)---C(37)	1.44(2)
C(14)---C(15)	1.38(2)	C(33)---C(34)	1.38(2)
C(15)---C(16)	1.42(2)	C(34)---C(35)	1.35(2)
C(21)---C(22)	1.42(2)	C(35)---C(36)	1.42(2)
C(21)---C(26)	1.41(2)	C(37)---O(31)	1.23(1)
C(22)---C(23)	1.38(2)	C(37)---O(32)	1.38(1)
C(22)---C(27)	1.48(2)	C---H _{calc}	0.98(0)

Table A3.2 Final thermal parameters for $\text{PhP}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}]_2$

Atom	U 1 1	U 2 2	U 3 3	U 2 3	U 1 3	U 1 2	
P(1)	0.022(2)	0.023(2)	0.015(2)	0.005(2)	0.008(2)	-0.002(2)	
Atom	U	Atom	U	Atom	U	Atom	U
C(11)	0.018(3)	C(22)	0.018(3)	O(21)	0.032(3)	C(35)	0.038(4)
C(12)	0.023(3)	C(23)	0.024(4)	O(22)	0.026(2)	C(36)	0.029(4)
C(13)	0.030(4)	C(24)	0.036(4)	C(31)	0.010(3)	C(37)	0.026(4)
C(14)	0.035(4)	C(25)	0.022(3)	C(32)	0.020(3)	O(31)	0.030(2)
C(15)	0.032(4)	C(26)	0.022(3)	C(33)	0.029(4)	O(32)	0.021(2)
C(16)	0.021(3)	C(27)	0.025(4)	C(34)	0.037(4)	H	0.050(0)
C(21)	0.016(3)						

Table A3.3 Bond angles for $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$ (°).

C(11)-P(1)-C(21)	120.1(5)	C(23)-C(22)-C(27)	127(1)
C(11)-P(1)-O(22)	90.1(5)	C(22)-C(23)-C(24)	119(1)
C(11)-P(1)-C(31)	118.7(5)	C(23)-C(24)-C(25)	119(1)
C(11)-P(1)-O(32)	90.3(5)	C(24)-C(25)-C(26)	122(1)
C(21)-P(1)-O(22)	88.2(5)	C(21)-C(26)-C(25)	117(1)
C(21)-P(1)-C(31)	121.2(5)	C(22)-C(27)-O(21)	125(1)
C(21)-P(1)-O(32)	91.0(5)	C(22)-C(27)-O(22)	112(1)
O(22)-P(1)-C(31)	91.3(4)	O(21)-C(27)-O(22)	122(1)
O(22)-P(1)-O(32)	179.2(5)	P(1)-O(22)-C(27)	115.8(8)
C(31)-P(1)-O(32)	89.1(4)	P(1)-C(31)-C(32)	110.6(8)
P(1)-C(11)-C(12)	117.9(9)	P(1)-C(31)-C(36)	128.1(9)
P(1)-C(11)-C(16)	120.8(9)	C(32)-C(31)-C(36)	121(1)
C(12)-C(11)-C(16)	121(1)	C(31)-C(32)-C(33)	120(1)
C(11)-C(12)-C(13)	118(1)	C(31)-C(32)-C(37)	115(1)
C(12)-C(13)-C(14)	120(1)	C(33)-C(32)-C(37)	124(1)
C(13)-C(14)-C(15)	121(1)	C(32)-C(33)-C(34)	117(1)
C(14)-C(15)-C(16)	118(1)	C(33)-C(34)-C(35)	121(1)
C(11)-C(16)-C(15)	119(1)	C(34)-C(35)-C(36)	121(1)
P(1)-C(21)-C(22)	112.2(8)	C(31)-C(36)-C(35)	117(1)
P(1)-C(21)-C(26)	128.6(9)	C(32)-C(37)-O(31)	128(1)
C(22)-C(21)-C(26)	119(1)	C(32)-C(37)-O(32)	110(1)
C(21)-C(22)-C(23)	121(1)	O(31)-C(37)-O(32)	120(1)
C(21)-C(22)-C(27)	111(1)	P(1)-O(32)-C(37)	114.3(7)

Table A3.4 Final positional parameters for $\text{PhP}[\text{C}_6\text{H}_4\text{COO}]_2$

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
P(1)	0.1257(1)	0.0511(4)	0.3454(2)	C(26)	0.0370(5)	0.253(2)	0.3744(8)
C(11)	0.1203(4)	-0.071(2)	0.2466(8)	C(27)	0.1669(5)	0.315(2)	0.2904(8)
C(12)	0.1667(5)	-0.145(2)	0.2256(8)	O(21)	0.1982(3)	0.404(1)	0.2597(6)
C(13)	0.1625(5)	-0.243(2)	0.1519(9)	O(22)	0.1774(3)	0.164(1)	0.3048(6)
C(14)	0.1142(5)	-0.266(2)	0.1003(9)	C(31)	0.1705(4)	-0.010(1)	0.4419(7)
C(15)	0.0687(5)	-0.189(2)	0.1183(9)	C(32)	0.1445(5)	-0.108(1)	0.4955(8)
C(16)	0.0715(5)	-0.093(1)	0.1952(8)	C(33)	0.1715(5)	-0.166(2)	0.5765(8)
C(21)	0.0872(4)	0.231(1)	0.3462(7)	C(34)	0.2254(5)	-0.134(2)	0.5956(9)
C(22)	0.1147(4)	0.362(1)	0.3167(8)	C(35)	0.2509(5)	-0.041(2)	0.5423(9)
C(23)	0.0931(5)	0.511(2)	0.3145(8)	C(36)	0.2244(5)	0.021(2)	0.4613(8)
C(24)	0.0438(5)	0.533(2)	0.3431(8)	C(37)	0.0884(5)	-0.129(2)	0.4672(8)
C(25)	0.0166(5)	0.405(1)	0.3713(8)	O(31)	0.0563(3)	-0.208(1)	0.5028(5)
				O(32)	0.0738(3)	-0.059(1)	0.3860(5)
H(12)	0.2010(5)	-0.128(2)	0.2621(8)	H(24)	0.0284(5)	0.639(2)	0.3437(8)
H(13)	0.1943(5)	-0.296(2)	0.1362(9)	H(25)	-0.0187(5)	0.423(1)	0.3897(8)
H(14)	0.1120(5)	-0.339(2)	0.0499(9)	H(26)	0.0172(5)	0.165(2)	0.3957(8)
H(15)	0.0352(5)	-0.201(2)	0.0788(9)	H(33)	0.1527(5)	-0.227(2)	0.6175(8)
H(16)	0.0393(5)	-0.043(1)	0.2119(8)	H(34)	0.2454(5)	-0.179(2)	0.6490(9)
H(23)	0.1123(5)	0.600(2)	0.2925(8)	H(35)	0.2885(5)	-0.016(2)	0.5598(9)
				H(36)	0.2435(5)	0.083(2)	0.4209(8)

APPENDIX FOUR

NMR SPECTRA FOR $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{COMe})$

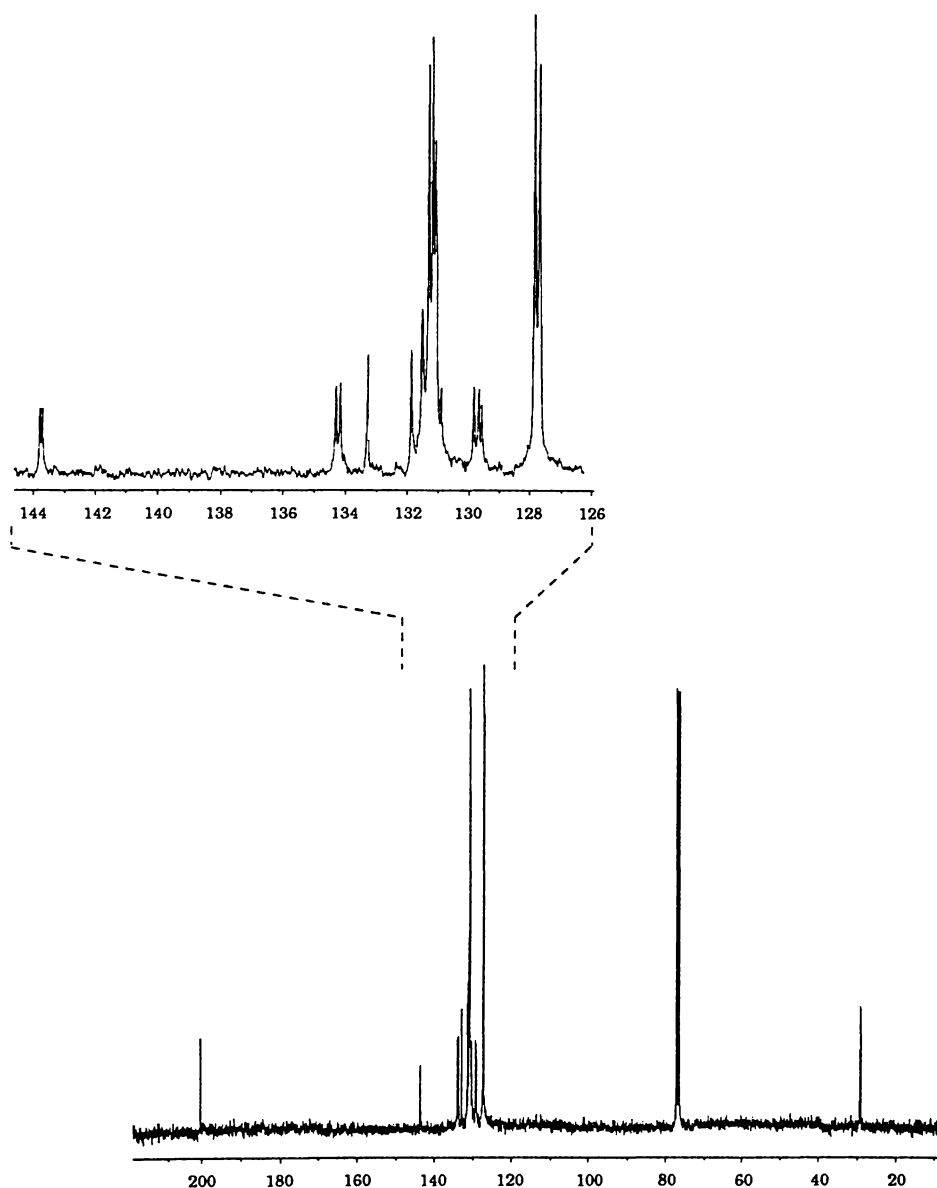


Figure A4.1 ^{13}C nmr spectrum of diphenyl-2-acetylphenylphosphane.

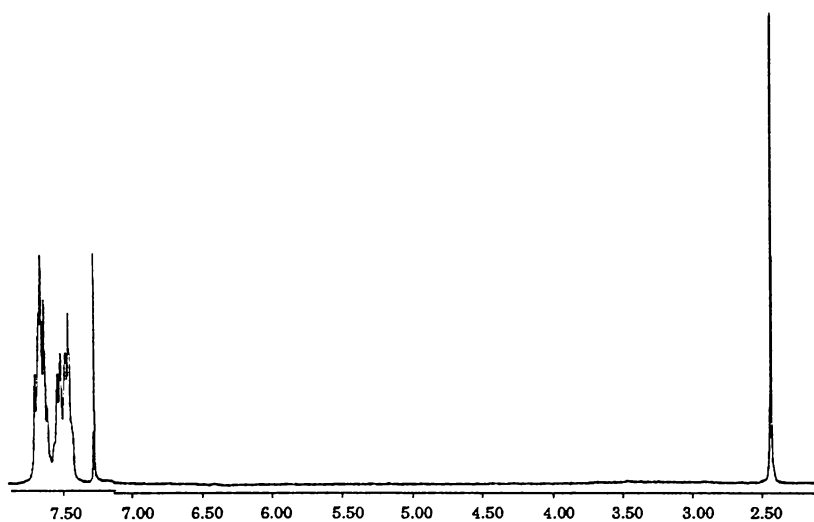


Figure A4.2 ^1H nmr spectrum of diphenyl-2-acetylphenylphosphane.

APPENDIX FIVE

POSITIONAL, THERMAL AND BOND LENGTH DATA FOR $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})$

Table A5.1 Bond lengths for $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})\cdot\frac{1}{2}\text{C}_7\text{H}_{16}$
(pm).

Ru(1)---Ru(2)	283.6(2)	C(32)---O(32)	116(2)
Ru(1)---Ru(3)	294.7(2)	C(41)---C(42)	137(2)
Ru(1)---P(1)	233.9(4)	C(41)---C(46)	141(2)
Ru(1)---C(11)	194(2)	C(42)---C(43)	143(2)
Ru(1)---C(12)	189(2)	C(42)---C(47)	147(2)
Ru(1)---C(13)	195(2)	C(43)---C(44)	140(2)
Ru(1)---C(14)	220(1)	C(44)---C(45)	138(2)
Ru(2)---Ru(3)	292.6(2)	C(45)---C(46)	137(2)
Ru(2)---C(14)	202(2)	C(47)---C(48)	150(2)
Ru(2)---C(21)	194(2)	C(47)---O(47)	123(2)
Ru(2)---C(22)	186(2)	C(51)---C(52)	140(0)
Ru(2)---C(23)	193(2)	C(51)---C(56)	140(0)
Ru(3)---P(1)	232.8(4)	C(52)---C(53)	140(0)
Ru(3)---C(31)	184(2)	C(53)---C(54)	140(0)
Ru(3)---C(32)	193(1)	C(54)---C(55)	140(0)
Ru(3)---C(41)	208(1)	C(55)---C(56)	140(0)
Ru(3)---O(47)	212(1)	C(61)---C(62)	140(0)
P(1)---C(51)	183.1(7)	C(61)---C(66)	140(0)
P(1)---C(61)	181.3(9)	C(62)---C(63)	140(0)
C(11)---O(11)	114(2)	C(63)---C(64)	140(0)
C(12)---O(12)	116(2)	C(64)---C(65)	140(0)
C(13)---O(13)	114(2)	C(65)---C(66)	140(0)
C(14)---O(14)	116(2)	C(71)---C(71)	153(4)
C(21)---O(21)	116(2)	C(71)---C(72)	150(2)
C(22)---O(22)	119(2)	C(72)---C(73)	154(3)
C(23)---O(23)	115(2)	C(73)---C(74)	124(4)
C(31)---O(31)	115(2)	C---H _{calc}	98(0)

Table A5.2 Bond angles for $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})\cdot\frac{1}{2}\text{C}_7\text{H}_{16}$ (°).

Ru(2)-Ru(1)-Ru(3)	60.80(0)	P(1)-Ru(3)-C(32)	173.0(4)
Ru(2)-Ru(1)-P(1)	111.4(1)	P(1)-Ru(3)-C(41)	98.1(4)
Ru(2)-Ru(1)-C(11)	86.5(4)	P(1)-Ru(3)-O(47)	86.2(3)
Ru(2)-Ru(1)-C(12)	142.3(4)	C(31)-Ru(3)-C(32)	91.8(6)
Ru(2)-Ru(1)-C(13)	89.9(4)	C(31)-Ru(3)-C(41)	95.4(6)
Ru(2)-Ru(1)-C(14)	45.1(4)	C(31)-Ru(3)-O(47)	172.3(5)
Ru(3)-Ru(1)-P(1)	50.7(1)	C(32)-Ru(3)-C(41)	87.6(5)
Ru(3)-Ru(1)-C(11)	90.6(4)	C(32)-Ru(3)-O(47)	91.1(5)
Ru(3)-Ru(1)-C(12)	157.0(4)	C(41)-Ru(3)-O(47)	77.6(5)
Ru(3)-Ru(1)-C(13)	87.9(4)	Ru(1)-P(1)-Ru(3)	78.3(1)
Ru(3)-Ru(1)-C(14)	105.9(4)	Ru(1)-P(1)-C(51)	118.4(3)
P(1)-Ru(1)-C(11)	92.9(4)	Ru(1)-P(1)-C(61)	119.2(4)
P(1)-Ru(1)-C(12)	106.3(4)	Ru(3)-P(1)-C(51)	120.9(3)
P(1)-Ru(1)-C(13)	88.7(4)	Ru(3)-P(1)-C(61)	119.9(4)
P(1)-Ru(1)-C(14)	156.6(4)	C(51)-P(1)-C(61)	100.9(5)
C(11)-Ru(1)-C(12)	90.9(6)	Ru(1)-C(11)-O(11)	176(1)
C(11)-Ru(1)-C(13)	176.4(6)	Ru(1)-C(12)-O(12)	178(1)
C(11)-Ru(1)-C(14)	86.9(5)	Ru(1)-C(13)-O(13)	177(1)
C(12)-Ru(1)-C(13)	91.7(6)	Ru(1)-C(14)-Ru(2)	84.3(5)
C(12)-Ru(1)-C(14)	97.1(6)	Ru(1)-C(14)-O(14)	137(1)
C(13)-Ru(1)-C(14)	90.4(5)	Ru(2)-C(14)-O(14)	138(1)
Ru(1)-Ru(2)-Ru(3)	61.50(0)	Ru(2)-C(21)-O(21)	173(1)
Ru(1)-Ru(2)-C(14)	50.6(4)	Ru(2)-C(22)-O(22)	177(1)
Ru(1)-Ru(2)-C(21)	94.2(4)	Ru(2)-C(23)-O(23)	176(1)
Ru(1)-Ru(2)-C(22)	149.0(4)	Ru(3)-C(31)-O(31)	176(1)
Ru(1)-Ru(2)-C(23)	94.5(4)	Ru(3)-C(32)-O(32)	166(1)
Ru(3)-Ru(2)-C(14)	112.1(4)	Ru(3)-C(41)-C(42)	113(1)
Ru(3)-Ru(2)-C(21)	88.1(4)	Ru(3)-C(41)-C(46)	130(1)
Ru(3)-Ru(2)-C(22)	149.5(4)	C(42)-C(41)-C(46)	116(1)
Ru(3)-Ru(2)-C(23)	88.9(4)	C(41)-C(42)-C(43)	122(1)
C(14)-Ru(2)-C(21)	97.5(6)	C(41)-C(42)-C(47)	116(1)
C(14)-Ru(2)-C(22)	98.4(6)	C(43)-C(42)-C(47)	120(2)
C(14)-Ru(2)-C(23)	94.4(6)	C(42)-C(43)-C(44)	118(2)
C(21)-Ru(2)-C(22)	88.9(6)	C(43)-C(44)-C(45)	118(2)
C(21)-Ru(2)-C(23)	168.0(6)	C(44)-C(45)-C(46)	122(2)
C(22)-Ru(2)-C(23)	87.8(6)	C(41)-C(46)-C(45)	121(2)
Ru(1)-Ru(3)-Ru(2)	57.70(0)	C(42)-C(47)-C(48)	123(2)
Ru(1)-Ru(3)-P(1)	51.0(1)	C(42)-C(47)-O(47)	116(1)
Ru(1)-Ru(3)-C(31)	96.5(4)	C(48)-C(47)-O(47)	119(1)
Ru(1)-Ru(3)-C(32)	122.5(4)	Ru(3)-O(47)-C(47)	116.3(9)
Ru(1)-Ru(3)-C(41)	147.1(4)	P(1)-C(51)-C(52)	122.3(3)
Ru(1)-Ru(3)-O(47)	88.0(3)	P(1)-C(51)-C(56)	117.7(3)
Ru(2)-Ru(3)-P(1)	108.7(1)	C(5n)-C(5n)-C(5n)	120.00(0)
Ru(2)-Ru(3)-C(31)	97.0(4)	P(1)-C(61)-C(62)	120.9(3)
Ru(2)-Ru(3)-C(32)	64.8(4)	P(1)-C(61)-C(66)	119.0(3)
Ru(2)-Ru(3)-C(41)	150.0(4)	C(6n)-C(6n)-C(6n)	120.00(0)
Ru(2)-Ru(3)-O(47)	90.8(2)	C(71)-C(72)-C(73)	113(2)
P(1)-Ru(3)-C(31)	91.6(5)	C(72)-C(73)-C(74)	113(3)

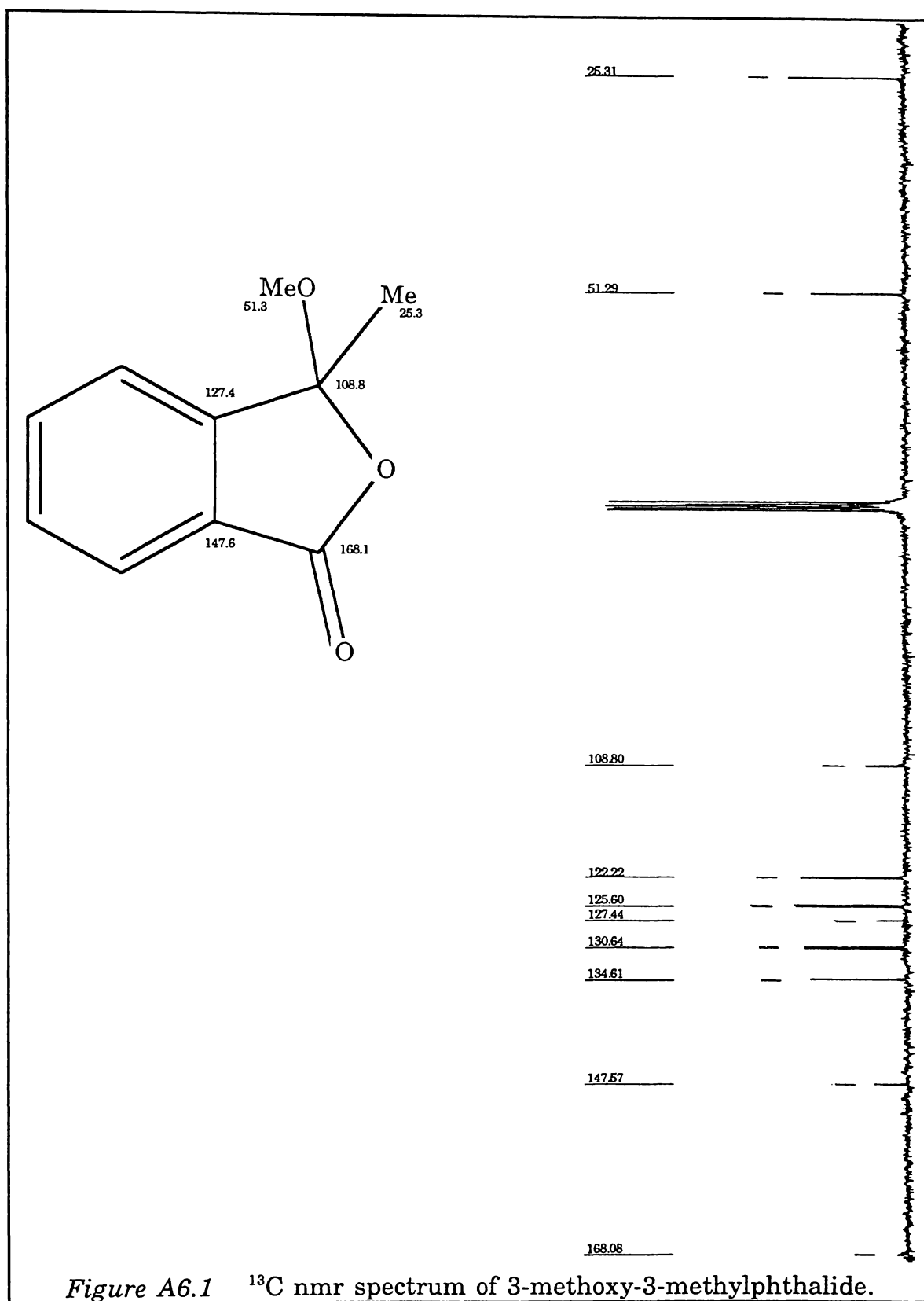
Table A5.3 Final positional parameters for
 $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})\cdot\frac{1}{2}\text{C}_7\text{H}_{16}$

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
Ru(1)	0.3959(1)	0.2648(1)	0.1423(1)	C(52)	0.348(1)	0.4950(6)	0.3881(6)
Ru(2)	0.4984(1)	0.0324(1)	0.2017(1)	C(53)	0.391(1)	0.5907(6)	0.4038(6)
Ru(3)	0.3385(1)	0.1798(1)	0.3472(1)	C(54)	0.415(1)	0.6763(6)	0.3288(6)
P(1)	0.2696(4)	0.3620(3)	0.2719(3)	C(55)	0.395(1)	0.6661(6)	0.2382(6)
C(11)	0.237(2)	0.214(1)	0.123(1)	C(56)	0.351(1)	0.5704(6)	0.2224(6)
C(12)	0.390(2)	0.372(1)	0.033(1)	C(61)	0.0886(8)	0.4208(8)	0.2762(7)
C(13)	0.560(2)	0.306(1)	0.164(1)	C(62)	0.0337(8)	0.4418(8)	0.1933(7)
C(14)	0.522(2)	0.119(1)	0.069(1)	C(63)	-0.1073(8)	0.4788(8)	0.1991(7)
C(21)	0.331(2)	-0.017(1)	0.199(1)	C(64)	-0.1935(8)	0.4948(8)	0.2877(7)
C(22)	0.598(2)	-0.111(1)	0.170(1)	C(65)	-0.1386(8)	0.4738(8)	0.3706(7)
C(23)	0.664(2)	0.061(1)	0.229(1)	C(66)	0.0025(8)	0.4368(8)	0.3649(7)
C(31)	0.485(2)	0.222(1)	0.3785(9)	C(71)	-0.048(2)	0.058(2)	1.002(1)
C(32)	0.399(1)	0.022(1)	0.3946(9)	C(72)	-0.010(2)	0.146(2)	0.920(1)
O(11)	0.145(1)	0.188(1)	0.1066(8)	C(73)	-0.114(2)	0.261(2)	0.923(2)
O(12)	0.384(1)	0.438(1)	-0.0350(7)	C(74)	-0.102(5)	0.320(3)	0.983(3)
O(13)	0.654(1)	0.3331(9)	0.1759(8)	H(43)	-0.116(2)	0.181(1)	0.566(1)
O(14)	0.581(1)	0.1021(8)	-0.0076(8)	H(44)	-0.064(2)	0.228(1)	0.708(1)
O(21)	0.234(1)	-0.0541(9)	0.2048(7)	H(45)	0.161(2)	0.251(1)	0.705(1)
O(22)	0.662(1)	-0.2004(8)	0.1467(9)	H(46)	0.330(2)	0.235(1)	0.5668(9)
O(23)	0.765(1)	0.072(1)	0.2458(9)	H(481)	-0.124(2)	0.094(1)	0.439(1)
O(31)	0.571(1)	0.2520(9)	0.4016(7)	H(482)	-0.058(2)	0.094(1)	0.327(1)
O(32)	0.421(1)	-0.0653(8)	0.4408(7)	H(483)	-0.145(2)	0.210(1)	0.368(1)
C(41)	0.210(2)	0.200(1)	0.4799(9)	H(52)	0.331(1)	0.4349(6)	0.4408(6)
C(42)	0.082(2)	0.181(1)	0.483(1)	H(53)	0.405(1)	0.5978(6)	0.4675(6)
C(43)	-0.024(2)	0.192(1)	0.567(1)	H(54)	0.446(1)	0.7435(6)	0.3399(6)
C(44)	0.007(2)	0.219(1)	0.649(1)	H(55)	0.412(1)	0.7262(6)	0.1855(6)
C(45)	0.138(2)	0.234(1)	0.647(1)	H(56)	0.337(1)	0.5633(6)	0.1587(6)
C(46)	0.238(2)	0.224(1)	0.5654(9)	H(62)	0.0943(8)	0.4305(8)	0.1311(7)
C(47)	0.055(2)	0.157(1)	0.393(1)	H(63)	-0.1459(8)	0.4936(8)	0.1409(7)
C(48)	-0.081(2)	0.138(1)	0.382(1)	H(64)	-0.2926(8)	0.5209(8)	0.2918(7)
O(47)	0.153(1)	0.1445(7)	0.3258(7)	H(65)	-0.1991(8)	0.4851(8)	0.4329(7)
C(51)	0.328(1)	0.4849(6)	0.2974(6)	H(66)	0.0410(8)	0.4220(8)	0.4231(7)

Table A5.4 Final thermal parameters for
 $\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\eta^2\text{-C}_6\text{H}_4\text{COMe})\frac{1}{2}\text{C}_7\text{H}_{16}$

Atom	U11	U22	U33	U23	U13	U12	
Ru(1)	0.0292(9)	0.0256(7)	0.0175(7)	-0.0017(5)	-0.0061(6)	-0.0128(6)	
Ru(2)	0.0310(9)	0.0262(7)	0.0232(7)	-0.0040(5)	-0.0077(6)	-0.0100(6)	
Ru(3)	0.0270(8)	0.0222(7)	0.0181(7)	-0.0020(5)	-0.0052(6)	-0.0112(6)	
P(1)	0.033(3)	0.021(2)	0.026(2)	-0.005(2)	-0.006(2)	-0.008(2)	
C(11)	0.02(1)	0.019(8)	0.025(8)	0.003(6)	0.009(8)	-0.004(7)	
C(12)	0.03(1)	0.04(1)	0.023(8)	-0.005(8)	0.000(8)	-0.012(8)	
C(13)	0.015(9)	0.025(8)	0.035(9)	-0.004(7)	-0.008(8)	-0.006(7)	
C(14)	0.03(1)	0.05(1)	0.032(9)	-0.026(8)	-0.006(8)	-0.011(8)	
C(21)	0.06(1)	0.012(8)	0.026(8)	-0.003(6)	0.001(9)	-0.016(9)	
C(22)	0.04(1)	0.06(1)	0.030(9)	0.009(8)	-0.017(8)	-0.03(1)	
C(23)	0.03(1)	0.019(8)	0.04(1)	-0.002(7)	-0.008(9)	-0.005(8)	
C(31)	0.04(1)	0.037(9)	0.013(8)	-0.003(7)	-0.004(8)	-0.008(9)	
C(32)	0.03(1)	0.026(9)	0.027(8)	0.003(7)	-0.014(7)	-0.013(7)	
O(11)	0.043(8)	0.060(8)	0.066(8)	-0.008(6)	-0.021(7)	-0.022(7)	
O(12)	0.09(1)	0.061(8)	0.027(6)	0.013(6)	-0.015(7)	-0.006(7)	
O(13)	0.044(8)	0.053(7)	0.062(8)	0.001(6)	-0.018(7)	-0.025(7)	
O(14)	0.046(8)	0.046(7)	0.039(7)	-0.024(6)	-0.002(6)	-0.003(6)	
O(21)	0.045(8)	0.046(7)	0.047(7)	-0.016(6)	0.002(6)	-0.025(6)	
O(22)	0.050(8)	0.021(6)	0.09(1)	-0.020(6)	-0.006(7)	0.007(6)	
O(23)	0.05(1)	0.09(1)	0.070(9)	-0.040(8)	-0.017(8)	-0.007(8)	
O(31)	0.034(7)	0.051(7)	0.042(7)	0.000(5)	-0.025(6)	-0.019(6)	
O(32)	0.08(1)	0.022(6)	0.038(7)	0.007(5)	-0.010(7)	0.000(6)	
C(41)	0.04(1)	0.020(8)	0.026(8)	0.002(6)	-0.004(8)	-0.010(8)	
C(42)	0.05(1)	0.022(8)	0.032(9)	0.007(7)	-0.001(8)	-0.008(8)	
C(43)	0.02(1)	0.04(1)	0.05(1)	-0.006(8)	0.003(8)	-0.004(8)	
C(44)	0.06(1)	0.05(1)	0.04(1)	-0.010(9)	0.02(1)	-0.02(1)	
C(45)	0.05(1)	0.031(9)	0.04(1)	-0.001(8)	-0.01(1)	-0.004(9)	
C(46)	0.04(1)	0.028(8)	0.018(8)	-0.003(7)	-0.009(8)	-0.004(8)	
C(47)	0.04(1)	0.027(9)	0.05(1)	-0.005(8)	-0.016(9)	-0.004(8)	
C(48)	0.04(1)	0.06(1)	0.06(1)	-0.011(9)	-0.015(9)	-0.02(1)	
O(47)	0.030(7)	0.026(6)	0.030(6)	-0.007(5)	-0.008(5)	-0.005(5)	
C(71)	0.06(2)	0.10(2)	0.05(1)	-0.01(1)	-0.02(1)	-0.04(1)	
C(72)	0.05(1)	0.09(2)	0.07(1)	0.01(1)	-0.02(1)	-0.02(1)	
C(73)	0.10(2)	0.05(1)	0.11(2)	-0.02(1)	-0.05(2)	0.01(1)	
C(74)	0.10(4)	0.01(2)	0.14(4)	-0.04(2)	-0.02(3)	0.01(2)	
Atom	U	Atom	U	Atom	U	Atom	U
C(51)	0.023(3)	C(54)	0.044(4)	C(61)	0.036(4)	C(64)	0.070(6)
C(52)	0.044(4)	C(55)	0.044(4)	C(62)	0.052(5)	C(65)	0.074(6)
C(53)	0.048(5)	C(56)	0.028(4)	C(63)	0.067(6)	C(66)	0.052(5)
H	0.050(0)						

APPENDIX SIX



APPENDIX SEVEN

POSITIONAL, THERMAL AND BOND LENGTH DATA FOR $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$

Table A7.1 Bond angles for $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ (°).

Cl(1)-Mn(1)-Cl(2)	84.6(2)	C(22)-Mn(2)-C(23)	87(1)
Cl(1)-Mn(1)-P(1)	82.8(2)	Mn(1)-Cl(1)-Mn(2)	94.7(2)
Cl(1)-Mn(1)-C(11)	95.9(7)	Mn(1)-Cl(2)-Mn(2)	93.8(2)
Cl(1)-Mn(1)-C(12)	174.9(8)	Mn(2)-P(2)-P(1)	104.7(1)
Cl(1)-Mn(1)-C(13)	90.5(8)	Mn(2)-P(2)-C(201)	115.3(5)
Cl(2)-Mn(1)-P(1)	86.7(2)	Mn(2)-P(2)-C(211)	120.3(6)
Cl(2)-Mn(1)-C(11)	176.2(8)	P(1)-P(2)-C(201)	106.1(6)
Cl(2)-Mn(1)-C(12)	90.8(8)	P(1)-P(2)-C(211)	103.3(5)
Cl(2)-Mn(1)-C(13)	90.5(8)	C(201)-P(2)-C(211)	105.7(7)
P(1)-Mn(1)-C(11)	97.1(8)	Mn(1)-P(1)-P(2)	104.2(3)
P(1)-Mn(1)-C(12)	94.8(8)	Mn(1)-P(1)-C(101)	121.7(5)
P(1)-Mn(1)-C(13)	172.9(8)	Mn(1)-P(1)-C(111)	112.7(6)
C(11)-Mn(1)-C(12)	88(1)	P(2)-P(1)-C(101)	103.1(5)
C(11)-Mn(1)-C(13)	85(1)	P(2)-P(1)-C(111)	109.4(5)
C(12)-Mn(1)-C(13)	91(1)	C(101)-P(1)-C(111)	105.0(7)
Cl(1)-Mn(2)-Cl(2)	84.7(2)	Mn(1)-C(11)-O(11)	178(2)
Cl(1)-Mn(2)-P(2)	86.2(2)	Mn(1)-C(12)-O(12)	175(2)
Cl(1)-Mn(2)-C(21)	91.2(7)	Mn(1)-C(13)-O(13)	178(2)
Cl(1)-Mn(2)-C(22)	175.6(7)	Mn(2)-C(21)-O(21)	175(2)
Cl(1)-Mn(2)-C(23)	88.6(8)	Mn(2)-C(22)-O(22)	173(2)
Cl(2)-Mn(2)-P(2)	83.8(2)	Mn(2)-C(23)-O(23)	177(2)
Cl(2)-Mn(2)-C(21)	174.9(8)	P(2)-C(201)-C(202)	118.5(4)
Cl(2)-Mn(2)-C(22)	95.8(7)	P(2)-C(201)-C(206)	121.5(4)
Cl(2)-Mn(2)-C(23)	89.1(8)	P(2)-C(211)-C(212)	118.4(5)
P(2)-Mn(2)-C(21)	93.0(8)	P(2)-C(211)-C(216)	121.5(5)
P(2)-Mn(2)-C(22)	98.2(7)	P(1)-C(101)-C(102)	119.9(4)
P(2)-Mn(2)-C(23)	171.5(8)	P(1)-C(101)-C(106)	120.1(4)
C(21)-Mn(2)-C(22)	88(1)	P(1)-C(111)-C(112)	119.8(5)
C(21)-Mn(2)-C(23)	93(1)	P(1)-C(111)-C(116)	120.1(5)

Table A7.2 Bond lengths for $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$ (pm).

Mn(1)---Cl(1)	238.7(6)	P(1)---P(2)	233.5(8)
Mn(1)---Cl(2)	243.6(7)	P(1)---C(101)	184(1)
Mn(1)---P(1)	237.7(7)	P(1)---C(111)	185(1)
Mn(1)---C(11)	177(2)	P(2)---C(201)	187(1)
Mn(1)---C(12)	176(2)	P(2)---C(211)	183(1)
Mn(1)---C(13)	180(3)	C(11)---O(11)	121(2)
Mn(2)---Cl(1)	241.7(7)	C(12)---O(12)	118(2)
Mn(2)---Cl(2)	240.4(6)	C(13)---O(13)	118(3)
Mn(2)---P(2)	235.6(7)	C(21)---O(21)	119(2)
Mn(2)---C(21)	178(2)	C(22)---O(22)	117(2)
Mn(2)---C(22)	179(2)	C(23)---O(23)	113(3)
Mn(2)---C(23)	186(3)	C(Ph)---C(Ph)	140(0)
		C(Ph)---H(Ph)	98(0)

Table A7.3 Final positional parameters for $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
Mn(1)	0.2336(4)	0.1916(3)	0.9167(3)	Mn(2)	0.2384(4)	0.4465(3)	0.7874(3)
Cl(1)	0.3486(6)	0.3811(5)	0.9528(4)	Cl(2)	0.0959(5)	0.2720(5)	0.7755(4)
P(1)	0.3639(6)	0.1656(5)	0.7803(4)	P(2)	0.3506(6)	0.3270(5)	0.6850(5)
C(11)	0.327(2)	0.135(2)	1.025(2)	O(11)	0.388(2)	0.094(1)	1.100(1)
C(12)	0.144(2)	0.054(2)	0.878(2)	O(12)	0.091(2)	-0.040(1)	0.856(1)
C(13)	0.140(3)	0.230(2)	1.020(2)	O(13)	0.076(2)	0.255(1)	1.086(1)
C(21)	0.355(2)	0.569(2)	0.801(2)	O(21)	0.426(1)	0.654(1)	0.807(1)
C(22)	0.151(2)	0.501(2)	0.672(2)	O(22)	0.097(2)	0.549(1)	0.603(1)
C(23)	0.143(3)	0.522(2)	0.878(2)	O(23)	0.085(2)	0.564(1)	0.936(1)
C(101)	0.534(1)	0.166(1)	0.821(1)	C(102)	0.606(1)	0.143(1)	0.738(1)
C(103)	0.736(1)	0.148(1)	0.768(1)	C(104)	0.794(1)	0.175(1)	0.881(1)
C(105)	0.722(1)	0.197(1)	0.963(1)	C(106)	0.592(1)	0.193(1)	0.933(1)
C(111)	0.309(1)	0.033(1)	0.680(1)	C(112)	0.378(1)	-0.060(1)	0.684(1)
C(113)	0.332(1)	-0.163(1)	0.613(1)	C(114)	0.219(1)	-0.173(1)	0.538(1)
C(115)	0.150(1)	-0.079(1)	0.535(1)	C(116)	0.195(1)	0.024(1)	0.606(1)
C(201)	0.516(1)	0.389(1)	0.683(1)	C(202)	0.597(1)	0.425(1)	0.785(1)
C(203)	0.719(1)	0.474(1)	0.786(1)	C(204)	0.761(1)	0.488(1)	0.686(1)
C(205)	0.680(1)	0.452(1)	0.584(1)	C(206)	0.557(1)	0.402(1)	0.582(1)
C(211)	0.284(1)	0.264(1)	0.5402(8)	C(212)	0.355(1)	0.197(1)	0.4813(8)
C(213)	0.305(1)	0.143(1)	0.3729(8)	C(214)	0.184(1)	0.156(1)	0.3235(8)
C(215)	0.112(1)	0.223(1)	0.3824(8)	C(216)	0.162(1)	0.277(1)	0.4908(8)
H(102)	0.562(1)	0.122(1)	0.652(1)	H(103)	0.792(1)	0.130(1)	0.705(1)
H(104)	0.894(1)	0.178(1)	0.904(1)	H(105)	0.766(1)	0.218(1)	1.050(1)
H(106)	0.536(1)	0.210(1)	0.997(1)	H(112)	0.466(1)	-0.053(1)	0.741(1)
H(113)	0.385(1)	-0.235(1)	0.616(1)	H(114)	0.184(1)	-0.252(1)	0.483(1)
H(115)	0.062(1)	-0.087(1)	0.477(1)	H(116)	0.142(1)	0.096(1)	0.603(1)
H(202)	0.564(1)	0.414(1)	0.863(1)	H(203)	0.782(1)	0.502(1)	0.865(1)
H(204)	0.856(1)	0.527(1)	0.687(1)	H(205)	0.712(1)	0.463(1)	0.506(1)
H(206)	0.494(1)	0.375(1)	0.503(1)	H(212)	0.449(1)	0.187(1)	0.5196(8)
H(213)	0.360(1)	0.091(1)	0.3273(8)	H(214)	0.145(1)	0.115(1)	0.2396(8)
H(215)	0.018(1)	0.234(1)	0.3442(8)	H(216)	0.107(1)	0.329(1)	0.5364(8)

Table A7.4 Final thermal parameters for
 $\text{Mn}_2(\mu\text{-}\eta^1, \eta^1\text{-Ph}_2\text{PPPh}_2)(\mu\text{-Cl})_2(\text{CO})_6$

Atom	U11	U22	U33	U23	U13	U12
Mn(1)	0.030(3)	0.024(2)	0.020(2)	0.009(2)	0.000(2)	-0.007(2)
Mn(2)	0.033(3)	0.021(2)	0.018(2)	0.003(2)	0.005(2)	-0.004(2)
Cl(1)	0.044(4)	0.025(3)	0.021(3)	-0.002(3)	0.006(3)	-0.006(3)
Cl(2)	0.029(4)	0.026(3)	0.028(3)	0.010(3)	0.004(3)	-0.002(3)
P(1)	0.030(4)	0.027(4)	0.020(3)	0.003(3)	-0.002(3)	-0.001(3)
P(2)	0.044(5)	0.021(4)	0.022(3)	0.002(3)	0.003(3)	-0.005(3)

Atom	U	Atom	U	Atom	U	Atom	U
C(11)	0.031(6)	C(204)	0.039(6)	C(101)	0.026(6)	C(114)	0.047(7)
C(12)	0.038(6)	C(205)	0.032(6)	C(102)	0.040(7)	C(115)	0.027(5)
C(13)	0.046(7)	C(206)	0.024(5)	C(103)	0.054(8)	C(116)	0.038(6)
C(21)	0.032(6)	C(211)	0.024(5)	C(104)	0.040(6)	O(11)	0.040(4)
C(22)	0.028(6)	C(212)	0.029(6)	C(105)	0.029(6)	O(12)	0.046(5)
C(23)	0.052(7)	C(213)	0.039(7)	C(106)	0.027(6)	O(13)	0.044(4)
C(201)	0.023(5)	C(214)	0.034(6)	C(111)	0.033(6)	O(21)	0.031(4)
C(202)	0.033(6)	C(215)	0.037(6)	C(112)	0.039(6)	O(22)	0.039(4)
C(203)	0.029(6)	C(216)	0.032(6)	C(113)	0.041(7)	O(23)	0.048(5)
H	0.050(0)						

APPENDIX EIGHT

CRYSTAL AND POSITIONAL DATA FOR $\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_8$

Table A8.1 Crystal data for $\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_8$.

Molecular formula : $\text{C}_8\text{Cl}_2\text{Mn}_2\text{O}_8$

M = 404.890

Crystal class : Monoclinic

Space group : $\text{P}2_1/c$

a = 9.322(5) *U* = 1264(2)

b = 11.404(8) *Z* = 4

c = 12.629(10) *F*(000) = 776

β = 109.57(5) *D*_{calc} = 2.13 g cm⁻³

X-rays : Mo-K_α (λ = 0.710 69 Å)

Temperature of collection : -100°C

Linear absorption coefficient (μ) : 20.56 cm⁻¹

During the course of this study the structure of $\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_8$ was redetermined by X-ray crystal structure analysis. The crystal data is given in Table A8.1 and the final positional parameters in Table A8.2. There were no significant differences from the previous determination.^[1]

1 Clegg W. and Morton S., *Acta. Cryst.*, B34 (1978), 1707.

<i>Table A8.2</i> Final positional parameters for $\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_8$							
Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
Mn(1)	0.5940(1)	0.1202(0)	0.3247(0)	O(23)	0.1949(3)	0.2812(2)	0.4196(2)
Mn(2)	0.1889(1)	0.1262(0)	0.2232(0)	O(24)	0.1909(4)	-0.0282(3)	0.0304(2)
Cl(1)	0.3877(1)	0.0087(1)	0.3453(1)	C(11)	0.7351(4)	0.0233(3)	0.4176(3)
Cl(2)	0.3947(1)	0.2388(1)	0.2034(1)	C(12)	0.5868(4)	0.0283(3)	0.1986(3)
O(11)	0.8265(3)	-0.0365(2)	0.4752(2)	C(13)	0.5957(4)	0.2126(3)	0.4497(3)
O(12)	0.5853(3)	-0.0241(2)	0.1217(2)	C(14)	0.7425(4)	0.2088(3)	0.3034(3)
O(13)	0.6019(3)	0.2688(3)	0.5251(2)	C(21)	0.0469(4)	0.2197(3)	0.1273(3)
O(14)	0.8377(3)	0.2643(2)	0.2911(2)	C(22)	0.0418(5)	0.0363(3)	0.2455(3)
O(21)	0.0439(3)	0.2762(2)	0.0658(3)	C(23)	0.1939(4)	0.2226(3)	0.3470(3)
O(22)	0.0544(3)	-0.0184(2)	0.2578(3)	C(24)	0.1933(4)	0.0302(3)	0.1033(3)